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IN ENGLISH TRANSLATION



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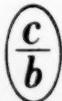
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CARBOXYMETHYLCELLULOSE - ITS CHEMICAL AND PHYSICOCHEMICAL PROPERTIES

G. A. Petropavlovskii

The decisions of the XXIst Congress of the CPSU and the May Plenum of the Central Committee of the CPSU (1958) provided for an extensive development program of the chemical industry of our country. The production of various cellulose derivatives and their industrial uses should therefore increase considerably. Among the numerous derivatives of cellulose, water- and alkali-soluble cellulose ethers have recently become very prominent; these include methylcellulose, ethylcellulose, hydroxyethylcellulose, ethylhydroxyethylcellulose, hydroxypropylcellulose, the sodium salt of cellulose sulfate, and many others. However, it is hardly possible to cite examples of such extensive utilization and industrial production as has been the case for carboxymethylcellulose in recent years. In the United States alone 10,000-12,000 tons of sodium carboxymethylcellulose is used annually [1]. As is known, its main field of utilization is in detergent production, and it is also used in the petroleum, pharmaceutical, paper, textile, food, and many other industries.

Sodium carboxymethylcellulose is made by treatment of alkali cellulose with monochloroacetic acid or its sodium salt. This reaction is clearly analogous to the formation of ethylglycolic acid from monochloroacetic acid and sodium ethylate, and the product was therefore often called celluloseglycolic acid. Since the structural formula of carboxymethylcellulose shows that one hydrogen atom in the methyl group is replaced by carboxyl, subsequently this compound was given the name of carboxymethylcellulose,* and this is the term widely used at the present time.

In commercial types of CMC the degree of substitution varies from 0.5 to 1.2 carboxyl groups per anhydroglucose unit. The average degree of polymerization of such samples is in the range of 300-3000.

The distribution of substituent groups (carboxymethyl) in various CMC samples was studied by Timell and Spurlin [2]. They showed that the CMC molecular chain contains unsubstituted, monosubstituted, and disubstituted anhydroglucose units. It was found that in all the samples studied only one of two neighboring secondary hydroxyl groups in cellulose is substituted by a carboxymethyl radical. They attribute this to the influence of repulsion forces between negatively charged chloroacetate ions and carboxymethyl groups in positions 2 or 3.

Similarly, steric and electrostatic considerations indicate that simultaneous substitution of hydroxyl groups in positions 2, 3, and 6 cannot be expected.

Timell [3] also studied the relative reactivity of hydroxyl groups in the reaction of alkali cellulose with monochloroacetic acid. He prepared 10 CMC samples, with degrees of substitution from 0.2 to 0.36, the water solubility of which increased from 0.08 to 29.65%. In these original CMC samples the ratio of substituted primary hydroxyl groups to the number of secondary hydroxyl groups was in the range of 0.92-1.35. Thus, in the range of degrees of substitution studied, the ratio of substituted primary hydroxyls to secondary hydroxyls was roughly unity in all cases. This suggests that in the carboxymethylation reaction the primary hydroxyl groups of cellulose are approximately twice as reactive as the secondary.

* For brevity, we use the following notation: CMC for carboxymethylcellulose; H-CMC for the free acid, and Na-CMC for the sodium salt.

Properties of Carboxymethylcellulose in the Form of the Free Acid

The reaction of alkali cellulose with monochloroacetic acid, conducted in a strongly alkaline medium, yields the sodium salt of CMC. Therefore, if CMC is required as the free acid the reaction mass is treated with a solution of some mineral acid (HCl , H_2SO_4).

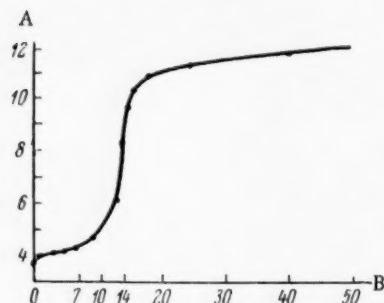


Fig. 1. Titration curve of CMC.
A) pH; B) number of milliliters of 0.1 N NaOH per 0.7954 g CMC.

CMC is insoluble in water, and can be washed in the solid form in running water to remove excess acidity and salts, without appreciable loss.

However, it is possible in special cases to prepare stable sols of CMC in water, containing about 1% or more of the solid substance.

The sodium salt can be obtained again by addition of caustic soda to these salts or to solid CMC. Other bases and ammonia also yield salts with CMC. CMC which has been dried for a long time at high temperatures is considerably more difficult to dissolve in alkali. Since anhydride and lactone bonds are unknown in compounds of this type, this fact must be due to condensation of the inner CMC structure during drying. Similar effects are observed generally when cellulose or its derivatives precipitated from aqueous solutions are dried.

The titration curve of CMC by NaOH is similar to the titration curve of a weak acid by a strong base, as shown in Fig. 1.

Calculations of the dissociation constant of CMC give values of about $5 \cdot 10^{-5}$ [4]. This value shows that carboxymethylcellulose is a moderately strong acid as compared with acetic acid, and a considerably stronger acid than carbonic or hydrocyanic. It is also interesting to note that if an aqueous solution of sodium CMC is acidified with some strong mineral acid, free CMC is precipitated over a wide range of pH, starting at pH = 6, and reaching completion only at pH = 2.5.

As already stated, stable aqueous dispersions of free carboxymethylcellulose can be prepared under special conditions. Dieckmann [5] showed that dispersions of this type, with high concentrations of the dispersed substance, can be prepared when aqueous solutions of Na- CMC are passed through cation-exchange resins of the strongly acid type.

The aqueous dispersions of CMC were slightly turbid viscous liquids, containing from 3 to 6% solid. The viscosity of these dispersions depended on the viscosity of the original Na- CMC solution, which varied between 8 and 10 centipoises (for 2% solutions) up to 1300- 2200 centipoises (for 1% solutions). Aqueous dispersions of CMC have good film-forming power. The mechanical properties of H- CMC films are given in Table 1.

TABLE 1
Mechanical Properties of H- CMC Films
Film Thickness 0.025 mm; Determinations at 21° and 50%
Relative Humidity; Starting Material of the Low-Viscosity Type

Properties	Unplasticized films	Plasticized films
Tensile strength (kg/mm ²)	4.98	4.2
Elongation at break (% of initial length)	2.7	2.3
Number of double folds	320	10,000
Glycerol content of film (%)	-	9

It is clear from Table 1 that H- CMC films have high mechanical strength — their tensile strength (in metric units) is about 5 kg/mm². The mechanical properties of H- CMC films can be varied by additions of

plasticizers. Such plasticizers as glycerol and dipropylene glycol, in 0.33 : 3.00 weight ratio of plasticizer to free acid, have good compatibility with H-CMC. Plasticizers considerably increase film flexibility without serious decrease of tensile strength.

H-CMC films dried to a water content below 15% do not dissolve in pure water between 0 and 100°. They are also insoluble in any organic solvent. However, the films are soluble in dilute aqueous alkalies ($\text{pH} \approx 11$) with formation of CMC salts.

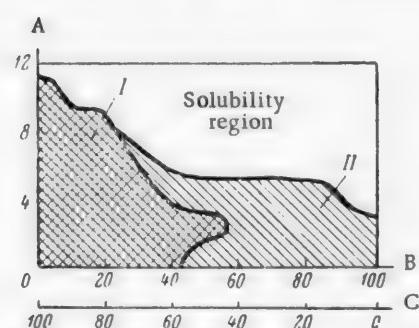


Fig. 2. Effects of drying conditions and solution pH on film solubility. A) pH; B) Na-CMC content (%); C) H-CMC content (%); insoluble films dried for 16 hours: I) at room temperature, II) at 105°.

already stated, films of 100% H-CMC are soluble only at and above $\text{pH} = 11$. Films of this composition may be used when it is desired to restrict their solubility within narrow pH ranges; for example, for coatings used for pharmaceutical preparations. Such a coating should not dissolve, for example, in weakly acid gastric juice but is readily soluble in the weakly alkaline medium of the intestinal tract.

Properties of Carboxymethylcellulose Salts

The sodium salt of CMC is the most important in the practical sense. The properties of this salt will be discussed in detail later in this paper. The potassium salt is in many respects similar to the sodium, and is readily soluble in water. The properties of its solutions are also similar to the properties of Na-CMC solutions. The ammonium salt of CMC is interesting because it is unstable and loses ammonia when heated between 50 and 60°. The lead, mercury, and aluminum salts of CMC are colorless, water-insoluble substances. The copper and nickel salts are light blue, and the iron salts are red. Salts of multivalent metals are as a rule insoluble in water, but other metallic salts are generally soluble. Any CMC salt may be prepared by treatment of H-CMC or Na-CMC with a solution of a salt of the particular metal. In some instances the reaction must be performed at a definite concentration and pH for isolation of the required salt.

Properties of the Sodium Salt of CMC

As already stated, Na-CMC is a most important cellulose derivative with extensive technical uses. In external appearance the pure product is a white fibrous material or powder, readily soluble in water at all temperatures. Na-CMC is highly hygroscopic.

According to Brown and Houghton [4], the substance contains about 11.5% moisture at 20° under normal laboratory conditions. When kept in a desiccator over dilute sulfuric acid in an atmosphere of 70% relative humidity, Na-CMC sorbed up to 42% water, equilibrium being attained after 14 days. If it was kept in an atmosphere saturated with water vapor, equilibrium was not reached even after 18 days, and up to 200% moisture (by weight) was absorbed.

After absorbing twice its own weight of water, Na-CMC does not change in external appearance. Addition of a large amount of water results in gel formation. On further dilution, when the concentration of the dry substance falls below 5-10%, a viscous solution is formed. Naturally, the formation of a gel and a fluid pseudoplastic

Film solubility can be varied within fairly wide limits by variations of pH, drying temperature, and film composition.

Figure 2 shows the influence of drying conditions and solution pH on the solubility of films made from mixtures of H-CMC and Na-CMC [5].

These films were prepared as follows. A solution of Na-CMC and a dispersion of H-CMC were mixed in definite proportions. Two films of equal thickness (0.025 mm) were made from each mixture. One film was then dried at room temperature for 16 hours, and the other at 105° for the same time. For the solubility determinations the films were cut in small pieces and immersed in aqueous buffer solutions of different pH. The amounts dissolved were determined after one hour at room temperature.

It follows from Fig. 2 that a film containing, say, 60% of the free acid and 40% of the sodium salt dissolves at $\text{pH} = 3.5$ and higher if it had been dried at room temperature. If a film is dried for 16 hours at 105°, it begins to dissolve only at $\text{pH} = 5.5$ and over. As

solution occurs at different concentrations which depend on the viscosity of Na- CMC. The utilization of Na- CMC solutions also depends on the viscosity type of the original product.

For some purposes, such as thickening of printing pastes, it is necessary to use very viscous solutions with the minimum contents of dissolved material. The high-viscosity type of CMC is required for this purpose. In other cases, as in use as adhesives and binders, the low-viscosity type of CMC may be used.

Viscosity of Na- CMC solutions. The most important property of the sodium salt of CMC is formation of highly viscous aqueous solutions. This property of many natural substances, including cellulose and rubber, is attributable to their molecular structure, which consists of very hydrophilic polymer chains.

The main factor influencing the viscosity of such solutions are the degree of polymerization, solution concentration, temperature, nature of the solvent and, in the case of ionic polymers, the pH of the medium.

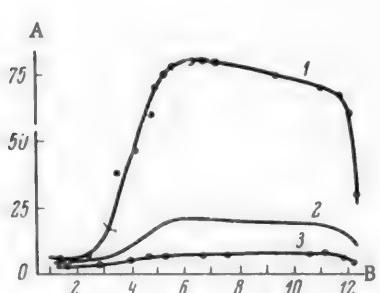


Fig. 3. Viscosity variations of 1% Na- CMC solution with the pH value.
A) Viscosity (centipoises); B) pH;
Solutions: 1) high viscosity, 2)
medium viscosity, 3) low viscosity.

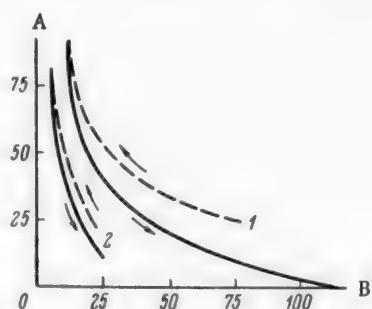


Fig. 4. Viscosity variations of 1% Na- CMC solution on heating and cooling. A) Temperature (in °C); B) viscosity (centipoises); Solutions: 1)
high viscosity, 2) medium viscosity.

We first consider the simplest viscosity relationships for solutions of CMC sodium salt. Figure 3 shows the influence of pH on the viscosity of aqueous solutions of this salt [4].

It is seen in Fig. 3 that the viscosity of Na- CMC solution has a maximum in the pH range from 6 to 9. It falls rapidly at pH below 6 because of gradual precipitation of free CMC, which is complete at pH \approx 2.5. At pH above 9 the solution viscosity also diminishes, slowly at first and then more rapidly when the pH reaches 11.5. However, the very considerable viscosity decrease in the strongly alkaline region is not due to precipitation of CMC, as it remains completely dissolved even at pH = 13.

An interesting fact is that these viscosity changes are reversible and that the original solution viscosity may be restored to its maximum value by addition of acid to bring the pH into the range of 6 to 9. Thus, alkali has a definite specific influence on viscosity.

It is now believed [6] that this effect can be attributed to changes in the configuration of CMC molecules in solution under the influence of an electrolyte. In absence of electrolyte the ionized groups of the polymer chain repel each other, so that the molecule tends to straighten out. On addition of electrolyte, its shielding effect diminishes repulsion between neighboring ionized groups of the polymer chain, and the molecule assumes a more coiled configuration.

Temperature also has a strong influence on the viscosity of Na- CMC solutions. If the solutions are heated to various temperatures and then cooled again, the heating and cooling curves exhibit hysteresis. This is illustrated in Fig. 4.

It is clear from Fig. 4 that the final viscosity of a Na- CMC solution, determined at room temperature after a heating- cooling cycle, is less than half the initial value.

The progressive decrease of viscosity with increase of temperature is also illustrated in Fig. 5 [4].

An aqueous (1%) solution of high-viscosity Na-CMC with initial viscosity of about 80 centipoises was heated at various temperatures for 20 minutes, and then cooled to the initial temperature. The viscosity was then determined again. It was found that the viscosity began to change at about 40-50°. The viscosity decrease grows rapidly with further increase of temperature to 100°.

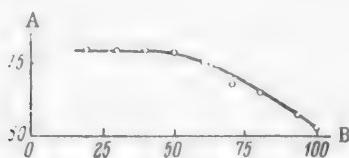


Fig. 5. Viscosity variations of 1% Na-CMC solution with the heating temperature. A) Viscosity (centipoises); B) temperature at which the solution was heated for 20 min.

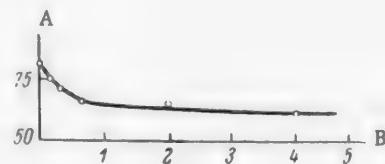


Fig. 6. Effect of heating time on the viscosity of 1% Na-CMC solution. A) Viscosity (centipoises); B) heating time (hours).

Figure 6 shows viscosity changes in relation to time of heating [4]. In these experiments a Na-CMC solution was heated for different times at 70°.

The initial viscosity of the solution was about 80 centipoises. After one hour of heating the viscosity fell to 65 centipoises. The subsequent viscosity decrease was slow, and after 4 hours of heating the viscosity was 61 centipoises. Thus, both heating time and temperature have a significant influence on the viscosity of Na-CMC solutions.

Recently Savage [7] also studied the effect of temperature on the viscosity of aqueous solutions of Na-CMC, and also of methylcellulose, hydroxyethylcellulose, and methylcarboxymethylcellulose.

The temperature-viscosity relationships of aqueous solutions of cellulose ethers are of great practical significance, as their use depends on them in many cases.

Thus, in applications of methylcellulose it must be taken into account that its aqueous solutions coagulate when heated. As has already been described, the viscosity-temperature relationship of aqueous Na-CMC solutions is of a different character. Such solutions do not undergo any coagulation when heated.

Savage plotted viscosity of Na-CMC solutions against temperature in semilogarithmic coordinates, and obtained a linear relationship. The viscosity-temperature relationship for such a solution on cooling is represented by a straight line which lies somewhat below the first. These experiments confirm the hysteresis of the viscosity-temperature relationship of Na-CMC solutions.

The decrease of viscosity is evidently the consequence of the very low relaxation rate in such polymeric systems as aqueous Na-CMC solutions. The time required to reach equilibrium in them may be very great, so that the system does not reach its original state in the measured time interval. There is also the possibility of some degradation of the molecules on heating; this, of course, should lead to irreversible changes of viscosity.

The modern views on solutions of cellulose derivatives in various solvents are based on the fact that these substances form true solutions in which the macromolecules are kinetically free. However, this does not exclude the fact that if an industrial product of cellulose etherification is extremely heterogeneous in its degree of etherification, some fractions of it would have low solubility. As a result, a solution might contain structural remains of the original cellulose together with a large amount of molecularly dispersed substance.

De Butts, Hudy, and Elliot [1] studied the flow properties of solutions of two CMC types, with degrees of substitution from 0.65 to 0.85. The first CMC sample in 1% aqueous solution (at 25°) had apparent viscosity from 1300 to 2200 centipoises, and the second, in 2% aqueous solution at the same temperature, from 300 to 600 centipoises. As the results of their determinations these authors obtained three types of flow diagrams corresponding to the following types of system: 1) pseudoplastic, 2) gel, and 3) thixotropic.

Concentrated solutions of carboxymethylcellulose, like solutions of many other high polymers, are non-Newtonian liquids, i.e., the rate of shear in such solutions is not directly proportional to the shearing stress.

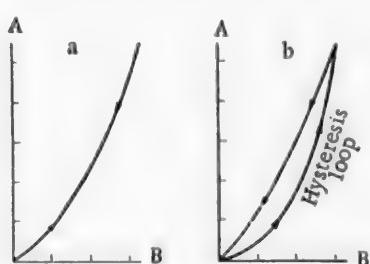


Fig. 7. Flow diagrams for a non-thixotropic pseudoplastic CMC solution [1] (a) and a thixotropic CMC solution [1] (b). A) Rate of shear; B) shear stress.

A plot of the rate of shear against the shearing stress for such flow gives a curve concave toward the shear rate axis (Fig. 7, a).

The apparent viscosity (ratio of the shearing stress to rate of shear) decreases with increasing rate of shear. This effect is independent of time for pseudoplastic systems. On the contrary, in thixotropic systems time is significant. The apparent viscosity diminishes with time if the rate of shear is constant. Under these conditions structural breakdown of the thixotropic material takes place within a measurable period of time. When the shearing stress is removed, the structure of the thixotropic material is restored. The time of such reversion may vary from a few seconds to several days, according to the system. The flow curve obtained by these authors for thixotropic solutions of carboxymethyl cellulose, with the aid of a rotational viscosimeter (first with increasing and then decreasing rotation rate) is shown in Fig. 7, b.

It must be pointed out that the region of the hysteresis loop under these conditions is a function of the time scale, and therefore all experimental conditions must be standardized if comparable results are to be obtained.

The flow curve of a thixotropic CMC solution with a gel structure is given in Fig. 8.

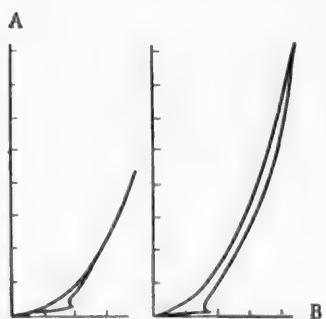


Fig. 8. Flow diagram [1] for a thixotropic solution of CMC with a gel structure. A) Rate of shear; B) shear stress.

This curve reveals the existence of a well-defined gel structure, which must be broken down before the solution flows.

This type of flow can be demonstrated visually. If such a solution is put in a vessel which is then inverted, the solution does not flow out, because of the considerable mechanical strength of the gel. If the vessel is shaken vigorously, the gel structure breaks down and flow similar to the flow of a thixotropic solution takes place, owing to the presence of a residual structure.

These results are interpreted [1] on the hypothesis that cellulose from which CMC is prepared contains both amorphous and crystalline regions. When alkali cellulose is prepared and subsequently etherified, uniform distribution of substituent groups along the cellulose chain cannot be expected, as the inner highly crystalline regions react more slowly than the others.

The solution therefore contains a small amount of nonmolecularly

dispersed CMC, i.e., aggregates of interconnected macromolecules, as in the oriented crystalline regions of the original cellulose. These crystallites act as gel centers, trapping a relatively large amount of molecularly dispersed CMC and forming a three-dimensional network by means of electrostatic or van der Waals forces. Dürig and Banderet [8] isolated such gel particles from Na-CMC solutions; x-ray investigations of these particles revealed a well-defined crystalline structure.

The foregoing leads to the conclusion that thixotropy of carboxymethylcellulose solutions is caused by the influence of gel centers. When the system is subjected to shear, some of the gel centers and their aggregates with individual macromolecules are broken down. This dispersion process occurs within measurable time, and therefore the apparent viscosity of the system diminishes with time. If the solution is left to stand, the gel centers may aggregate again. The apparent viscosity of the system then increases.

These interpretations by the above-named authors are confirmed by the fact that they obtained two phases by centrifugation of Na-CMC solutions under a centrifugal force 20,000 times the acceleration due to gravity. The first phase was a clear solution, and the second, a gelatinous residue. The flow diagram of the centrifugate is characteristic of pseudoplastic flow. The gel fraction exhibits pronounced thixotropy. The flow diagrams of these fractions are given in Fig. 9, a.

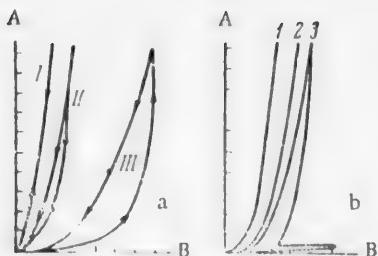


Fig. 9. Flow diagrams [1] of an original thixotropic CMC solution, centrifugate and gel fraction (a), and the system Fe^{3+} with CMC (b). A) Rate of shear; B) shear stress; I) centrifugate, II) original solution, III) gel; ratio of $\text{Fe}^{3+}/\text{COO}^-$: 1) 0, 2) 1/25, 3) 1/15.

As stated earlier, Na-CMC solutions have considerable anomalous viscosity. A characteristic feature of real Na-CMC solutions is the presence both of various nonmolecularly dispersed particles and of aggregates of macromolecules, especially in presence of multivalent cations. Therefore both in viscosimetric and in osmotic determinations of the degree of polymerization (DP) these peculiarities and the real composition of the solution must be taken into account, and fractions which falsify the results must be removed before the determinations.

Wurz [9] determined the molecular weight of Na-CMC by the osmotic method as follows.

Ordinary Na-CMC was extracted with 70% ethyl alcohol to remove NaCl, and dried for 2 hours at 105°. The washed product was dissolved in water to give a 0.5% solution. Solid sodium chloride was then added to the solution, to give a concentration of 2%. The solution was centrifuged for one hour to remove swollen particles, and the sol was carefully withdrawn by means of a pipet. The swollen particles in the centrifuge tube were washed three times with 2% sodium chloride solution. After removal of the last portion of the wash solution, the gelatinous residue on the bottom of the tube was washed with 70% ethyl alcohol until sodium chloride was completely removed, and was then dried and weighed. This gave an indirect determination of the concentration of the CMC sol. The molecular weight of the substance in these solutions was determined by means of the osmometer. The molecular weight was calculated from the Van't Hoff equation

$$M = \frac{RT}{\lim_{C \rightarrow 0} [P/C]} ,$$

with extrapolation of the osmotic pressure (determined at 0.5, 0.25, and 0.175% concentrations) to zero concentration C.

The results of experiments with seven different Na-CMC samples are given in Table 2.

The DP was determined by division of the molecular weight by the weight of the structural unit calculated for the given degree of etherification. After the molecular weights of several Na-CMC samples had been determined by the osmotic method, the samples were used as standards in viscosimetric determinations and calculations of the constant K_m .

These experiments showed that the most suitable solvent is 6% NaOH, because with considerable fluctuations of degree of polymerization of the samples and different degrees of etherification the fluctuations of the constant (K_m) in this solvent are not large, and are quite acceptable for technical determinations. Therefore, it may be taken that for Na-CMC solutions in 6% NaOH the constant $K_m = 6.6 \cdot 10^{-4}$. It must also be noted that the viscosity of alkaline solutions of Na-CMC did not decrease appreciably over 30 minutes. Recent, more systematic, observations showed that the quantitative relationship between intrinsic viscosity and molecular weight in the region of high degrees of polymerization must be represented, instead of by the equation

Further convincing confirmation of this hypothesis is provided by experiments on the influence of multivalent cations on the viscosity of nonthixotropic solutions of Na-CMC. The influence of trivalent iron (Fe^{3+}) on the flow of Na-CMC solutions is illustrated in Fig. 9, b. When the ratio of ferric to COO^- ions is 1 : 25 (Curve 2), there is an increase of viscosity, but no thixotropy or gelation, as the Fe concentration is not high enough for a three-dimensional structure to be formed in the solution. If the iron content of the solution is increased ($\text{Fe}^{3+}/\text{COO}^- = 1 : 15$), a distinct three-dimensional system is formed by cross linking.

This system is a relatively strong gel, which breaks down under shear to yield a highly thixotropic solution. Other metal ions, such as copper (Cu^{2+}) or aluminum (Al^{3+}), have a similar effect.

Determination of the Average Degree of Polymerization of Carboxymethylcellulose

$$[\eta] = K_m \cdot M \text{ by the equation } [\eta] = K \cdot M^\alpha,$$

where K and α are two constants, characteristic for a given system (solute—solvent). Schurz, Streizig, and Wurz [10] determined the constants K and α for Na-CMC solutions in 2% NaCl and 6% NaOH.

TABLE 2
Determination of Average Degree of Polymerization

Type of Na-CMC	Degree of etherifi- cation	$\lim_{C \rightarrow 0} \frac{P.C}{C}$	DP	Wt. of structural unit	Content of swollen particles (%)
1	0.5	0.72	185	201	0.33
2	0.7	0.51	240	218	1.0
3	0.7	0.28	440	218	42.6
4	0.5	0.27	500	201	5.6
5	0.95	0.215	520	238	0.02
6	0.7	0.23	540	218	9.66
7	1.0	0.145	705	242	0.93

For solutions of Na-CMC in 2% NaCl, K and α were found to be $2.33 \cdot 10^{-4}$ and 1.28, respectively. In 6% NaOH $K = 7.3 \cdot 10^{-3}$ and $\alpha = 0.93$. The value of α in 2% NaCl as solvent corresponds to rigid rodlike molecules. This configuration is the consequence of mutual repulsion of charges situated along the molecular chains.

The value of α in 6% NaOH corresponds to considerably more flexible and coiled chains. The increase of chain flexibility in 6% NaOH is due to weakened interaction between the charges on the chains owing to shielding. Therefore, the properties of carboxymethylcellulose in 6% NaOH as solvent must depend considerably less on the degree of substitution, which determines the charge density of the chains.

Determination of the Degree of Substitution (γ) of Carboxymethylcellulose

Determinations of γ for carboxymethylcellulose are based on different methods, but in the main these methods depend on various reactions of the carboxyl group. Methods based on titration of free CMC are the simplest and most rapid.

For example, the determination may be performed as follows [11]: a weighed sample of Na-CMC is shaken in a flask with 73% ethyl alcohol acidified with HCl (0.26 N HCl in the aqueous alcohol solution). At the end of a definite time the H-CMC is filtered off, washed with 75% ethyl alcohol to a neutral reaction and a negative reaction for chloride, and dried at 100°. A weighed sample of H-CMC is then dissolved in a definite volume of standard NaOH solution. When it is completely dissolved, excess NaOH is titrated by HCl with thymol blue indicator.

Other methods, such as determination of Na as NaCl (by ashing of Na-CMC and treatment of the ash with HCl) [12], conductometric titration of Na-CMC by acid [13], and calorimetric [13] and nephelometric [14] determinations, require the use of absolutely pure CMC. Methods free from this disadvantage are based on precipitation of copper salts of CMC [12, 15-17] and determination of copper in Cu-CMC, but they are time-consuming.

Dielectric Properties, Surface Activity, and Adsorption of Na-CMC

Allgen [18] studied aqueous solutions of Na-CMC at concentrations from 0.0025 to 0.1 g/liter, and obtained results which indicated considerable polarity of its molecules. Thus, the dielectric increment for 0.1% solution of Na-CMC in water was about 9 units. The shape of the curve for the dielectric constant as a function of Na-CMC concentration in solution showed strong interaction between the CMC molecules in solution, especially at concentrations above 0.01%. The calculated electrical moment for Na-CMC was about 1000 Debye units.

The high value for this moment is probably the result of combination of COO^- groups and the firmly-held Na^+ counterions. The least distance between Na^+ and COO^- (with the center of the negative charge between the oxygen atoms) is approximately 1.14 Å. In contrast to this, the dielectric moment for solutions of nonionic cellulose ethers (ethylhydroxyethylcellulose) and dextrin approached zero. The probable explanation of this effect is that the moment-carrying groups — OH and — O — in polysaccharides are in general distributed very symmetrically in the molecules, and therefore the total moment at right angles to the long axis of the molecule should be very small or zero.

The data presented above show that carboxymethylcellulose is a substance with a number of properties characteristic of many polyelectrolytes. The existence of a large electrical moment might be expected to lead to electrostatic adsorption in a number of cases. However, in view of the aggregation of CMC molecules on increase of concentration in solution, and of the shielding of the charges, electrostatic adsorption should occur mainly in dilute solutions. Certain experiments on the adsorption of CMC and its action as a stabilizing agent are considered below.

Investigations carried out in tests of Na-CMC as an addition to detergents showed that detergent properties are improved considerably by this product. Several authors [11] attribute this effect to fairly considerable adsorption of Na-CMC on cellulose fibers. Having a negatively charged polymer ion, carboxymethylcellulose increases considerably the weak negative charge of cellulose when adsorbed on the fiber. At the same time, a large proportion of dirt particles is also negatively charged in detergent solutions (at pH of about 7). Therefore adsorption of Na-CMC on fibers increases electrostatic repulsion between the fibers and the dirt particles which have already been removed from the fibers.

If this electrostatic hypothesis is correct, hydroxyethylcellulose and partially substituted methylcellulose should have only a weak effect. Ionic cellulose derivatives, such as sulfate esters, should have the same effect as carboxymethylcellulose. This is found to be the case in practice. The possibility of carboxymethylcellulose adsorption on cellulose fibers is in a number of cases explained by the fact that its macromolecules have the same structure as those of cellulose. Cohesion may lead to formation of hydrogen bonds between free OH groups in CMC and cellulose hydroxyls. With adsorption of this kind, washing with water should lead to easy desorption; this is also confirmed by experience. However, there are considerable objections to the explanation of the mechanism of the action of carboxymethylcellulose in terms of its adsorption on cellulose and increase of the electronegative charge on the fiber. Recent investigations with the aid of improved methods [19], including fluorescence analysis, have shown that carboxymethylcellulose is hardly adsorbed at all on cellulose fibers.

Some adsorption of Na-CMC occurs only at high concentrations (above 10%), in neutral and especially in acid media.

Investigations [20] with the aid of radioactive C^{14} isotope as tracer for the adsorption process showed that Na-CMC is weakly retained by wood cellulose. The retention of Na-CMC in the simple system Na-CMC — cellulose — water, in normal paper manufacture, was about 5-10%, and was almost independent of the degree of substitution in the range of γ from 119 to 39.

Only samples with limited solubility in water ($\gamma = 38$) were retained by wood cellulose to the extent of 60%. Addition of aluminum sulfate causes complete retention of Na-CMC; this is independent of the stoichiometric proportions of the amount of Al^{+++} necessary for complete retention of Na-CMC, and the amount of OCH_2COONa groups present in the CMC. In other words, the retention of Na-CMC is due not only to formation of an insoluble aluminum salt, but also to electrostatic adsorption of positively charged Al-CMC on the negatively charged cellulose fibers.

Surface-tension studies [21] of aqueous Na-CMC solutions at interfaces with air and nonaqueous liquids also showed that Na-CMC has very low surface activity. For example, the surface tension at the water—paraffin oil interface was 46.5–44.0 dynes/cm at 0.5% CMC concentration. When the Na-CMC concentration was 0.5%, the surface tension was 46.5–41.2 dynes/cm. These experiments are also consistent with data on the weak adsorption of CMC on various adsorbents, including bentonite and carbon black. Zavorokhina and Ben'kovskii [22] studied the adsorption of Na-CMC on various native and dialyzed clays. These experiments also showed that the adsorption of CMC is slight. In a number of instances negative values of adsorption were found by these workers. The explanation offered for the so-called negative adsorption was that adsorption of the solvent (water) was considerably greater than adsorption of carboxymethylcellulose in such cases.

There was virtually no adsorption of carboxymethylcellulose on dialyzed clays. Clay suspensions made from these clays and treated with CMC proved no worse (with regard to resistance to electrolytic coagulation) than suspensions made from the corresponding native clays, which adsorbed CMC. These authors therefore, considered that the stabilizing effect of Na-CMC consists not only of the formation of a structurized protective film (as the result of adsorption), but also of the creation of a highly viscous medium. Na-CMC increases the viscosity. The partial adsorption of CMC which occurs under certain conditions is possibly caused largely by its alcoholic hydroxyls, which are the active adsorption groups in CMC.

Biological Stability of Na-CMC

In many cases the utilization of carboxymethylcellulose necessitates evaluation of its biological stability. This applies to prolonged storage of its solutions, or of preparations with added CMC. The principal facts concerning the behavior of Na-CMC in presence of microorganisms are therefore summarized briefly below. It is believed that the stability of water-soluble cellulose ethers depends on the amount of substituent groups, at least one substituent in each glucose residue being needed for biological stability. Reese, Siu, and Lewinson [23] and others [24-26] showed that ordinary types of Na-CMC (degree of substitution 0.5-0.8) are readily fermented by many fungi. In a number of instances noncellulosic microorganisms grow on media containing CMC. However, Reese's experiments showed that with increase of the degree of substitution of Na-CMC from 0.5 to 1.2 its enzymatic hydrolysis by a culture of *Aspergillus fumigatus* is rapidly retarded, and is almost entirely arrested at degree of substitution 1.2.

Apart from the degree of substitution, the degree of polymerization and uniformity of substitution are important in relation to biological stability, samples of higher molecular weight and of greater uniformity being the more resistant to fermentation. Fractionation of Na-CMC into fractions of different DP has been described by Quinn and Karabinos [27].

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* Original Russian pagination. See C. B. Translation.

STUDY OF THE HYDRATION RATE OF MAGNESIUM OXIDE CALCINED AT DIFFERENT TEMPERATURES

P. P. Budnikov and Kh. S. Vorob'ev

Determination of the conditions for and rate of hydration of magnesium oxide, in relation to the calcination temperature, is extremely important with regard to the problem of increasing its content in Portland cement clinker. It is known that the presence of increased amounts of MgO in clinkers is a cause of breakdown of hardened cement.

The existing views on the influence of the calcination temperature, and therefore of the size of periclase crystals, on the rate of their hydration are not in full agreement. On the one hand, some workers, including Budnikov [1], Yasinovskii and Goncharov [2], and others, have shown that the hydration rate of MgO falls with increase of its calcination temperature, although very fine grinding may increase the tendency to hydration. On the other hand, Pirogov [3] and some others consider that highly-recrystallized periclase, calcined at high temperatures, has greater hydration activity than periclase of a low degree of recrystallization.

For studies of the effect of calcination temperature on the hydration rate of MgO, chemically pure MgO calcined at 800, 1200, 1300, 1400, and 1800° was taken. All the magnesium oxide samples were ground to pass completely through a 0085 sieve. The magnesium oxide powders were mixed either with water or with dilute (4%) magnesium chloride solution. Magnesium chloride was added in order to investigate its influence on the hydration of magnesium oxide. This additive had been found to have a favorable effect in hydration studies on high-magnesia Portland cements [4].

The amounts of water and magnesium chloride solution used for mixing were calculated to give pastes of normal consistency.

The degree of hydration of magnesium oxide was estimated from the amount of bound water, which was determined after the specimens had been kept for 1, 3, 30, and 360 days in a bath with a hydraulic seal, and also after autoclave treatment at 8 atmos for 4 hours. Bound water was determined by the usual method.

Degree of Hydration (%) of MgO Calcined at Different Temperatures

Hydration time (days)	800°			1200°			1300°			1400°			1800°		
	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	with water	with 4% MgCl ₂ solution	
1	75.40	81.60	6.48	56.42	14.62	50.20	4.72	5.24	3.95	6.91	—	—	—	—	
3	100.00	98.73	23.42	79.73	38.15	62.60	9.27	11.70	14.12	22.70	—	—	—	—	
30	99.82	100.00	94.76	99.60	69.50	95.72	32.80	84.40	36.40	60.75	—	—	—	—	
360	—	—	97.60	—	—	—	52.80	—	—	—	—	—	—	—	
4 hr (8 atm)	100.00	99.32	100.00	99.37	98.30	98.95	97.30	97.65	97.60	100.00	—	—	—	—	

The degrees of hydration of MgO mixed with water and with 4% MgCl₂ solution, calculated from the amounts of bound water, are given in the table.

It is clear from the table that the calcination temperature has a considerable effect on the hydration rate of MgO. Magnesium oxide calcined at 800° was more than 75% hydrated after only 1 day of moist storage, and hydration was complete after 3 days. Magnesium oxide calcined at 1200 and 1300° is hydrated slowly at first, but after 30 days of moist storage its degree of hydration reaches 70-95%. Further increase of the calcination temperature to 1400° sharply retards the hydration rate.

For example, magnesium oxide calcined at 1400° took up only 52.8% of the amount of water required for complete hydration after one year. Increase of the calcination temperature of MgO to 1800° did not reduce the hydration rate after 30 days as compared with MgO calcined at 1400°.

The effects of calcination temperature on the degree of hydration of magnesium oxide during moist storage and also in autoclave treatment are shown in Fig. 1, a. The use of 4% MgCl₂ solution for mixing with magnesium oxide accelerates the hydration of MgO in all cases. However, the accelerating effect of MgO differs for different calcination temperatures and at different hydration stages. Whereas the degree of hydration of MgO, calcined at 1400 and 1800° and kept under moist conditions for one day, increases by about 10-15% in presence of MgCl₂, the hydration of MgO calcined at 1200 or 1300° increases 3 to 8-fold.

The effect of MgCl₂ on the degree of hydration of MgO is shown in Fig. 1, b.

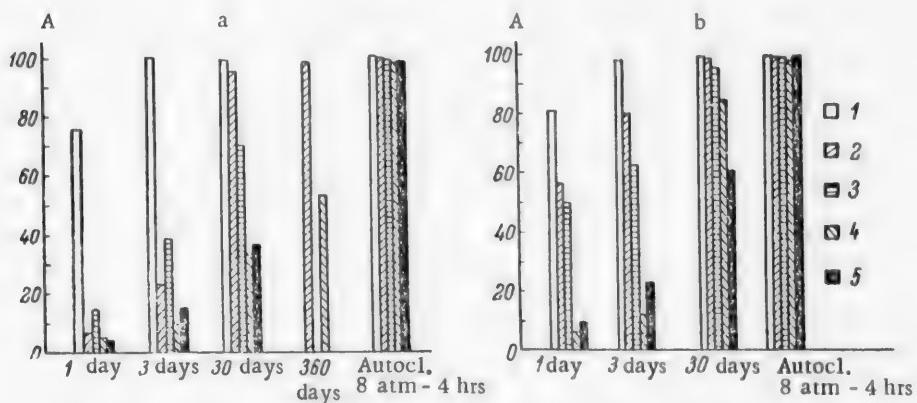


Fig. 1. Degree of hydration of MgO in relation to the calcination temperature and hydration time: a) mixed with water, b) mixed with 4% MgCl₂ solution.

A) Degree of hydration (%); calcination temperature (in °C): 1) 800, 2) 1200, 3) 1300, 4) 1400, 5) 1800.

In addition to determinations of bound water, thermograms of hydrated magnesium oxide were determined after definite storage times, by means of the Kurnakov recording pyrometer.

The purpose of these investigations was to detect decomposition reactions of the forming hydrates and carbonates, polymorphic transitions, and crystallization of newly formed compounds. The magnitude of the effects found should provide some confirmation of the estimated degree of hydration of MgO found from determinations of the amount of bound water. In addition, the thermograms should give an indication of the nature of the interaction between MgCl₂ and magnesium oxide, which results in accelerated hydration.

As is known, there are two different viewpoints on the influence of salts (electrolytes) on magnesium oxide during hydration. In one opinion, MgCl₂ and other salts exert a catalytic effect, and in the other, the formation of complex compounds (oxychlorides) is postulated.

Thermograms of hydrated magnesium oxide, calcined at different temperatures and stored under moist conditions for 1, 3, 30, and 360 days, and also treated in the autoclave, are given in Figs. 2-5.

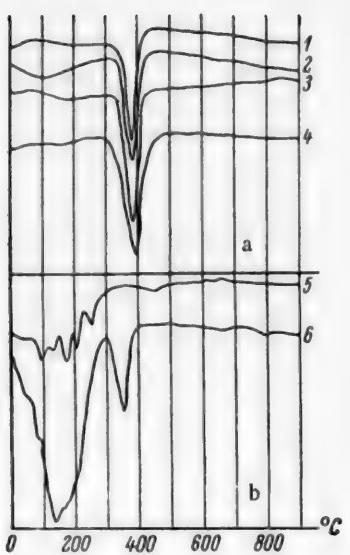


Fig. 2. Thermograms of: a) hydrated MgO calcined at 800° ; b) the salts $MgCl_2 \cdot 6H_2O$ (5) and $MgSO_4 \cdot 7H_2O$ (6); time of moist storage (days): 1) 1, 2) 3, 3) 30; 4) 8 atmos, 4 hours.

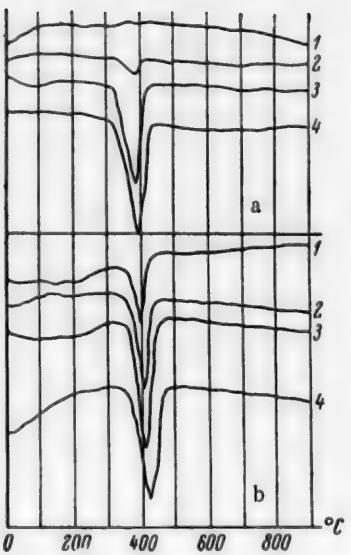


Fig. 3. Thermograms of hydrated MgO , calcined at 1200° : a) mixed with water, b) mixed with 4% $MgCl_2$ solution; hardening time (days): 1) 1, 2) 3, 3) 30; 4) 8 atmos, 4 hours.

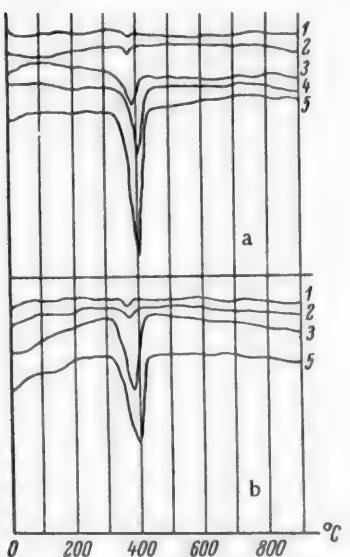


Fig. 4. Thermograms of hydrated MgO , calcined at 1400° : a) mixed with water, b) mixed with 4% $MgCl_2$ solution; hardening time (days): 1) 1, 2) 3, 3) 30, 4) 360; 5) 8 atmos, 4 hours.

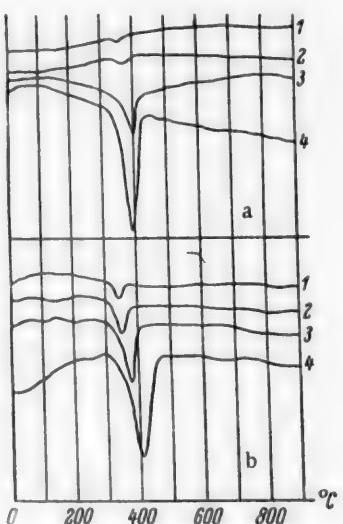


Fig. 5. Thermograms of hydrated MgO , calcined at 1800° : a) mixed with water, b) mixed with 4% $MgCl_2$ solution; hardening time (days): 1) 1, 2) 3, 3) 30; 4) 8 atmos, 4 hours.

These thermograms largely confirmed the results obtained in the earlier determinations of the amounts of bound water. Thermograms of hydrated MgO made with dilute MgCl₂ solution show that this additive has an accelerating effect on the hydration of MgO. However, these thermograms did not reveal any appreciable effects which would indicate the presence of new complex substances. Nevertheless, autoclave treatment of MgO samples mixed with 4% MgCl₂ solutions, which reached 95-97% hydration during moist storage, sometimes resulted in breakdown of these samples; this can be attributed to breakdown on the new compounds during autoclave treatment, and hydration of the MgO liberated from them.

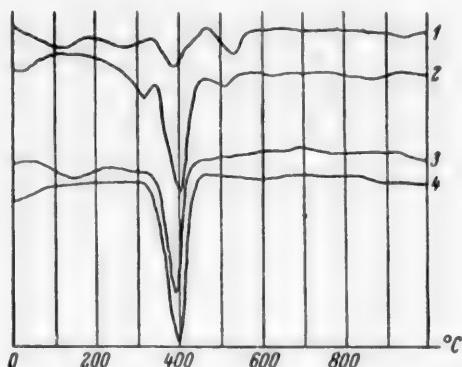


Fig. 6. Thermograms of hydrated MgO:
1, 2) mixed with 5% MgSO₄ solution;
3, 4) mixed with 15% MgCl₂ solution;
2, 4) autoclave treatment.

on the hydration of MgO, the thermograms in Fig. 6 suggest that here also the main reaction in the hydration of MgO is formation of Mg(OH)₂, and the degree of hydration of MgO increases considerably under the influence of a higher concentration of MgCl₂ solution. The endothermic effect at 110-130° may be attributed both to dehydration of MgCl₂·6H₂O and to composition of the unstable oxychloride. Autoclave treatment of magnesium oxide samples mixed with 5% MgSO₄ or 15% MgCl₂ solutions apparently leads to partial or total decomposition of the compounds formed; this is confirmed by decrease of the endothermic effect at 510° and increase of the main effect of Mg(OH)₂ dehydration.

SUMMARY

1. The degree of hydration of MgO decreases with increase of its calcination temperature.
2. Of the samples studied, magnesium oxide calcined at 1400° has the lowest tendency to hydration.
3. If dilute MgCl₂ solutions are used for mixing with magnesium oxide, the degree of early hydration is accelerated considerably, especially in the case of MgO calcined at 1200 and 1300°.
4. Small additions of MgCl₂ have mainly a catalytic effect in accelerating the reaction MgO + H₂O = Mg(OH)₂, but the possible formation of small amounts of oxychlorides is not excluded.
5. If MgO is mixed with magnesium sulfate solution, or with stronger solutions of magnesium chloride, thermal analysis reveals additional effects, indicative of the presence of other new compounds, apart from the main reaction of Mg(OH)₂ dehydration.
6. Autoclave treatment of the samples at 8 atmos results in almost complete (97-100%) hydration of MgO.

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THE PREPARATION OF ALUMINUM CARBONATE

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Aluminum carbonate has not been found in the earth's surface in the form of a mineral; neither has it been prepared or isolated as a definite chemical compound in the laboratory [1].

Hydrolysis is the main reason why aluminum carbonate cannot be obtained from its aqueous solutions. The degree of hydrolysis depends on the precipitation conditions; the interaction of solutions of potassium and aluminum sulfates with alkali-carbonate solutions on heating yields a precipitate of Al(OH)_3 which dissolves slowly in acids and which contains no carbon dioxide; if the reaction takes place in the cold, the precipitate has a different appearance and dissolves immediately in acids with evolution of CO_2 [2]. Aluminum carbonate is not formed when CO_2 is passed through Al_2O_3 solution, Al(OH)_3 being formed in this reaction [3].

Nevertheless, the amount of precipitated basic aluminum carbonates or the amount of carbon dioxide chemically combined with the precipitate increases if factors which intensify hydrolysis are eliminated. Therefore, in experiments on precipitation [4] the solutions used were cooled to 0° , and the precipitates were washed with absolute alcohol.

Basic aluminum carbonate, with the trade name Basaljel, is used in medicine [5]; a suspension of basic aluminum carbonates is used in production of paper for color photography, for increasing contrast [6].

We undertook a study of the conditions for the preparation of basic aluminum carbonate enriched with carbon dioxide.

The work was based on the following considerations.

1. Hydrolysis depends on temperature, and to reduce hydrolysis low temperatures should be used, which is inconvenient with aqueous media.

2. Hydrolysis also depends on the solution concentration. At low temperatures the solubility of aluminum salts on the one hand, and of alkali carbonates on the other, greatly decreases, i.e., the amount (concentration) of water in the system becomes considerable and can be reduced only to a definite limit.

3. The use of low temperatures is also necessary because, according to literature data [7], the vapor pressure of carbon dioxide in aluminum carbonate becomes appreciable even at $25\text{--}30^\circ$.

It was therefore considered desirable to carry out the precipitation in the water of crystallization, i.e., to bring about an ion-exchange reaction in the adsorption layers of crystalline hydrates:



Thereby it was possible to use lower temperatures with quite small amounts of water. In other words, hydrolysis could be reduced to a minimum. Moreover, under these conditions the duration of the ion-exchange process is greater than in precipitation in an aqueous medium.

The processes taking place under such conditions can be divided into two groups.

1. Processes taking place in water of crystallization, resembling reactions in the solid state. A chemical reaction between two substances in the crystalline state, when the number of points of contact is small (with only light stirring), cannot be expected to proceed at a measurable rate. The decisive role here is played by adsorption layers, which have the structure of solutions or melts in the case of readily soluble salts.

2. Processes taking place in adsorbed water. Crystalline hydrates such as $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, etc., which at room temperature have fairly low water-vapor pressures and are hygroscopic, are always surrounded by more or less thin adsorption layers, in which the water molecules are more "free" than water molecules in a typical crystal lattice. Such an adsorption layer also contains a certain amount of salt ions. The layer as a whole is therefore similar to a solution. In it take place ion-exchange processes represented by Eq. (1), accompanied by solution of ions of the other salt — alkali carbonate or ammonium carbonate. However, the chemical reaction results in release of molecules of "free" water, which increases the density of the adsorption layer and the amount of ions dissolved in it. The process therefore becomes, as it were, self-accelerated. Carbonates also have adsorption layers, containing molecules of "free" water.

The adsorption layers always contain water ions also, but the OH^- concentration in them is higher than the H^+ concentration. It is because of the excess of OH^- ions that pure aluminum carbonate cannot be obtained by precipitation in water of crystallization. However, it is important that the concentration of CO_3^{2-} ions should be much higher than the concentration of OH^- ions.

If the amount of adsorbed water is large, this is regarded as hygroscopic water, and in presence of this water ion exchange proceeds at a high rate.

In order to avoid hydrolysis, an attempt was made to use organic solvents, but, of course, carbonates are not soluble in common organic solvents. Several experiments in glycerol were unsuccessful.

Anhydrous aluminum salts (AlCl_3), sodium carbonate monohydrate, and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ were also tried, but satisfactory results were not obtained.

EXPERIMENTAL*

4.5 g of powdered $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 2 g of finely ground anhydrous sodium carbonate were taken. The two powders were put in a small basin and mixed by means of a glass rod. After a definite time the crystals began to deform owing to liberation of CO_2 . If the mixture was ground for a longer time in a mortar, it became moist with abundant liberation of carbon dioxide. If the mixture was not ground, but left at room temperature (or, even better, at 0°) for 2–3 days, and then washed thoroughly with cold water, a white precipitate was deposited rapidly on the bottom of the basin. Small crystals of indefinite shape could be seen under the microscope, but the precipitate had essentially a gel structure, and readily dissolved in dilute mineral acids with liberation of considerable amounts of CO_2 . Complete removal of SO_4^{2-} could not be achieved even by very prolonged washing of the precipitate, probably because of the presence of sparingly soluble basic aluminum sulfates, which are readily adsorbed by the precipitate.

Experiments with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. In the reaction, carried out in the water of crystallization, between aluminum nitrate and sodium or ammonium carbonates sodium or ammonium nitrate is formed; because of their considerable solubility in water, they can be easily washed out of the system. Aluminum nitrate is hygroscopic; to remove water, it should be dried for 30 minutes at 50 – 55° , and the drying is more complete if the salt is previously ground thoroughly. However, this salt is very hygroscopic and becomes moist again in air. The experiments were performed both with air-dry Na_2CO_3 and with $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

If finely ground anhydrous Na_2CO_3 is added in 25% excess at room temperature to finely ground $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ previously dried at 50° , and the two salts are mixed thoroughly with a glass rod, no visible changes take place in the system; no appreciable changes take place when the mixture is ground in a mortar, although it becomes somewhat moist. If the mixture is left to stand in a firmly stoppered flask, an intensive and self-accelerating process begins after several hours or several days, proceeding at room temperature with considerable evolution of CO_2 . The process can be retarded by the use of a refrigerator (the mixture then merely becomes slightly moist). Under these

* S. Venkova took part in the experimental work.

conditions condensation of considerable amounts of water vapor on the mixture should be avoided, otherwise it becomes very damp, and this hinders the experiment. The best results were obtained in winter in a cold room.

The substance prepared as described above was put in a mortar and ground thoroughly with addition of cold water containing pieces of ice. Sodium nitrate and excess sodium carbonate were removed from the solution by repeated grinding and decantation. The precipitate was transferred to a glass filter and washed repeatedly with cold water. The volume of wash water should be 15-20 times the volume of the reaction mixture. If bubbles of CO_2 are evolved when the substance is ground with ice water, this is a sign that ion exchange is not complete; aluminum hydroxide gel is formed, clogs the filter, and interferes with the preparation. At the end of the process a precipitate was obtained which was easily decanted and washed on the filter. The precipitate appeared crystalline under the microscope, but did not brighten with the use of crossed nicols. It was dried in air, over calcium chloride, and over P_2O_5 .

If ammonium carbonate is used instead of sodium carbonate, the ion-exchange reaction proceeds at a much higher rate in the crystals, and it is necessary to use low temperatures. The two powdered salts react immediately when mixed at room temperature, considerable amounts of CO_2 are evolved, and the system does not become moist as in the case of sodium carbonate. The rate of the ion-exchange process can be reduced at low temperatures. Thus, eventually a product with a high CO_2 content is obtained. It is washed with ice water, with repeated grinding and decantation. Thorough washing yields preparations containing only small amounts (traces) of ammonia.

Experiments with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The experimental procedure was the same as with aluminum nitrate. Preliminary drying of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is necessary to remove hygroscopic water. The wash waters were tested for chloride.

The CO_2 content was determined gravimetrically; the carbonate was decomposed by dilute H_2SO_4 , a stream of air free from CO_2 was passed through the system, and the liberated CO_2 was absorbed in askarit.

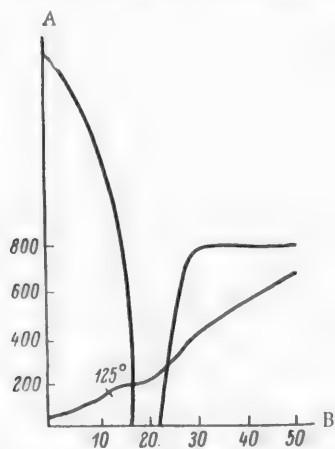


Figure. Differential heating curve (Experiment 32). A) Temperature (in $^{\circ}\text{C}$); B) time (minutes).

Aluminum was determined gravimetrically as Al_2O_3 , by precipitation with ammonia in an acid medium. Water and CO_2 were removed from the product by calcination, and Al_2O_3 was weighed ($\text{Al}_2\text{O}_3 + \text{Na}_2\text{O}$ in experiments with sodium carbonate).

The amounts of aluminum oxide obtained by precipitation and direct calcination were very close to the amounts obtained in the experiments with sodium carbonate; this shows that the preparations were satisfactorily free from Na_2CO_3 and NaNO_3 .

The results obtained by mixing of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and anhydrous Na_2CO_3 without special cooling in Experiment 11 are given below. The results of Experiment 32 were obtained at low temperatures by mixing of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

Experiment 11 Contents (in wt. %)

Al_2O_3	18.00
CO_2	5.84
H_2O	76.16

In view of the fact that the preparation was very moist, this weight composition corresponds to the formula $(\text{Al}_2\text{O}_3)_4 \cdot (\text{CO}_2)_3$.

Experiment 32 Contents (in wt. %)

Al_2O_3	21.50
CO_2	13.40
H_2O	65.10

If the water content is disregarded, this composition corresponds to $(\text{Al}_2\text{O}_3)_{2.10} \cdot (\text{CO}_2)_{3.05}$, or approximately $\text{Al}_2(\text{CO}_3)_3 \cdot 2\text{Al}(\text{OH})_3$.

It cannot be determined from the results of these experiments to what extent washing with cold water favors hydrolysis of the precipitated basic aluminum carbonate; it may be assumed that the hydrolysis is not too extensive because the precipitate is only slightly soluble. Cold water saturated with CO₂ in order to suppress hydrolysis was not used for washing.

For fuller characterization of the basic aluminum carbonates so prepared, heating curves were plotted with the aid of N. S. Kurnakov's differential pyrometer (see graph). These curves show a large endothermic effect at 125°. At this temperature basic aluminum carbonate undergoes thermal dissociation, with liberation of chemically-bound CO₂.

SUMMARY

1. An ion-exchange reaction in water of crystallization between crystalline Al(NO₃)₃·9H₂O and alkali (or ammonium) carbonate yields a precipitate containing considerable amounts of chemically-bound CO₂.

2. Differential thermal analysis was used to determine the temperature (125°) at which basic aluminum carbonate undergoes thermal dissociation with liberation of chemically-bound CO₂.

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PREPARATION OF SODIUM CARBONATE AND BICARBONATE BY MEANS OF ION EXCHANGERS

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At the present time ion-exchange resins are used mainly for extraction of ions from solutions of low concentrations, with the aims of purification (water softening or demineralization) or extraction of valuable components [1, 2].

Methods have recently been proposed for the production of sodium carbonate by means of ion exchangers [3], from fairly concentrated solutions; the processes proposed for the production of a solid product are so complicated that they are unlikely to be practicable.

It must be taken into account that in many cases sodium carbonate is used in solution; for such cases it is convenient to produce solutions of the required concentration at the utilization site. The ion-exchange method might prove suitable for this purpose. The availability of cheap soda solutions might stimulate organization of new industries; for example, native solutions of magnesium salts are not utilized in the Soviet Union—the precipitate formed by addition of lime is so hydrated and difficult to filter that this method is not used.

If magnesium is precipitated by sodium carbonate or bicarbonate on heating, a compact product of low water content which is easy to filter is formed. The use of solid soda for this purpose is uneconomic, but the production of soda solutions on the site might be justified.

Experiments were performed to clarify certain questions in this connection; the results are detailed below.

Dynamic Studies of Ion Exchange

In many publications on the dynamics of ion exchange the variations of the composition of the solution and ion exchanger with time and the position of the exchange zone in the column are represented by formulas which are so complicated that they are difficult to use for practical purposes [4].

Of great interest in this connection is the paper by Michaels [5], which contains a simplified method for calculation of ion-exchange dynamics in a column.

Ion exchange occurs in a relatively narrow exchange zone, which moves downward with flow of the liquid at a constant rate which depends on the liquid concentration and velocity, the specific capacity of the exchanger, and the selectivity coefficient of the exchanging ions.

Michaels regards the exchange zone to be the part of the column in which the concentration of the exchanged ion falls from 95 to 5% of its initial value (the inflection point on the elution curve).

If the ion exchanger is white and the ion is colored, the exchange zone may be observed visually; Michaels described a method for calculation of the zone height, its rate of descent, effective and total capacities, and other data.

A solution of known composition is passed through an ion-exchange column of known diameter and packing height.

Equal samples of effluent are collected and analyzed, and the results are used to plot the contents of the exchanged ion in the effluent (as % of the initial concentration) against effluent volume.

The following nomenclature is used:

A_{CS} , the column cross-sectional area, cm^2 ; r_T , the column radius (cm); h_T , height of bed in column (cm); V_T , total volume of effluent (cc); V_E , volume to break-through (cc); h_Z , height of exchange zone (cm); U_L , liquor velocity in column (cm/second); U_Z , rate of descent of exchange zone (cm/second); θ_T , total time from start to the second inflection point (seconds); θ_Z , time of descent of zone through a distance equal to the height of the exchange zone (seconds); θ_F , formation time of the exchange zone in the head of the column (seconds); Q_E , the area on the graph representing the number of meq adsorbed by the column up to break-through point (cm^2); Q_Z , the area on the graph representing the number of meq adsorbed in the exchange zone from the first to the second inflection point (cm^2); $Q_T = Q_E + Q_Z$; $Q_Z \text{ max}$, the area on the graph representing the total capacity of the column in the exchange zone (cm^2); F , fraction of the exchange capacity remaining free at break-through point; C_E , the effective capacity of the ion exchanger (meq/g); C_T , total capacity of the ion exchanger (meq/g).

The kinetic characteristics are calculated from the following formulas:

$$h_Z = U_Z \cdot \theta_Z = h_T \cdot \frac{\theta_Z}{\theta_T - \theta_F}, \quad (1)$$

$$U_Z = \frac{h_T}{\theta_T - \theta_F}, \quad (2)$$

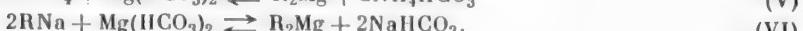
$$\theta_T = \frac{V_T}{U_L \cdot A_{CS}}, \quad (3)$$

$$F = \frac{Q_Z}{Q_Z \text{ max}} \quad (4)$$

$$\theta_F = (1 - F) \theta_Z \quad (5)$$

All the dynamic characteristics are calculated from experimental data, with the exception of θ_F , the time of zone formation, which is calculated on the basis of the following considerations: if $F = 0$, i.e., $Q_Z = 0$, this means that when the first inflection point (break-through) is reached, the total exchange capacity of the zone is utilized, the exchanger is saturated, and there is nothing more to be adsorbed, $Q_Z = 0$; hence, the time of zone formation is equal to the time required for the zone to descend through its own height. If $F = 1$, i.e., $Q_Z = Q_Z \text{ max}$, the time of zone formation when the first inflection point is reached is very short; these are limiting positions; in practice $\theta_F = (1 - F) \theta_Z$.

We studied the dynamics of ion exchange in systems which may be of significance in the production of sodium carbonate and bicarbonate solutions, with an admixture of magnesium chloride, from ammonium carbonate-bicarbonate and sodium chloride:



The results are given in Table 1.

The most important dynamic characteristics are the height of the ion-exchange zone, which is a measure of the binding of the solution ions by the ion exchanger, and the velocity of the exchange zone along the column, which depends on the capacity of the ion exchanger and is a measure of the working life of the column.

TABLE I
Experimental Data on the Dynamics of Ion Exchange

Exp. No.	Ion-exchange system	h_T (cm)	r_T (cm)	v_T (cm/sec)	Normality of influence solution	Grain size (mm)	θ_T (sec)	θ_Z (sec)	θ_F (sec)	F	ω_Z (cm)	C_T		
1	RH + NH ₄ OH	34	0.7	0.4	0.11	ESP	0.5	4220	974	568	0.417	8.76	0.009	1.9
2	RH + NH ₄ OH	32	0.7	0.4	0.11	KU1	0.5	5195	1403	777	0.445	9.82	0.007	2.41
3	RH + NH ₄ OH	53	1.1	0.086	0.11	SC	1.2—0.5	5814	1377	704	0.488	13.77	0.010	1.57
4	RNa + NH ₄ HCO ₃	58	1.4	0.024	0.10	SC	1.2—0.5	25250	6265	3189	0.491	16.29	0.0026	1.57
5	RNa + NH ₄ HCO ₃	32	0.7	0.1	0.22	KU1	0.5	3084	1785	937	0.475	26.77	0.015	2.1
6	RNH ₄ + KHCO ₃	57	0.75	0.04	0.10	SC	1.2—0.5	16098	8522	5684	0.333	46.8	0.0055	1.0
7	RNH ₄ + KHCO ₃	58	1.4	0.042	0.10	SC	1.2—0.5	16604	8771	4657	0.469	42.10	0.0048	1.6
8	RNH ₄ + NaHCO ₃	34	0.7	0.1	0.05	ESP	0.5	9415	6169	4330	0.298	40.7	0.0066	1.16
9	RNH ₄ + NaHCO ₃	32	0.7	0.1	0.06	KU1	0.5	11363	8272	5170	0.375	42.9	0.0052	1.17
10	R ₂ Mg + KHCO ₃	57	0.75	0.04	0.10	SC	1.2—0.5	13952	10037	6644	0.338	80.29	0.008	1.0
11	RNH ₄ + Mg(HCO ₃) ₂	57	0.79	0.04	0.12	SC	1.2—0.5	9343	4608	2788	0.395	40.08	0.0087	1.0
12	RNH ₄ + Mg(HCO ₃) ₂ + + 1 N NH ₄ Cl	58	1.4	0.04	0.02	SC	1.2—0.5	9085	8270	5516	0.333	134.3	0.016	0.1
13	RNa + Mg(HCO ₃) ₂ + + 1 N NaCl	58	1.4	0.04	0.02	SC	1.2—0.5	16604	14471	6309	0.564	81.0	0.0056	0.28
14	RNa + Mg(HCO ₃) ₂ + + 1 N NaCl	58	1.4	0.04	0.04	SC	1.2—0.5	9335	7456	3251	0.564	67.1	0.009	0.03

• Resins: ESP = espatite; SC = sulfonated coal; KU1 = cation exchanger.

TABLE 2
Ion Exchange Data for Sulfonated Coal in the Sodium Form

Column volume $\pi r^2 h$ (cm ³)	Volume rate V_L V _{col/hr}	Normality of		Normality of		Volume of sodium carbonate - bicarbonate (ml)	Yield of sodium carbonate-carbonates (meq/g)	Conversion of ammonium carbonates (%)
		influent		effluent				
		(NH ₄) ₂ CO ₃	NH ₄ HCO ₃	NaCl	Na ₂ CO ₃	NaHCO ₃	(NH ₄) ₂ CO ₃	
$\pi \cdot 1.12 \cdot 58 = 220$	{ 4.4 1.4 2.7	1.8 1.5 1.0	0 0 0	0 0.5 0.37	0.7 0.63 0	0 0 0.24	0.69 0.6 0.24	220 150 200
$\pi \cdot 0.752 \cdot 57 = 102$	{ 6 12 6 6 6 6 6 6 1.4	1.0 2.0 1.0 2.0 2.0 1 1 0 0.4	0 0 0 0 0 0 0 0.42	0.2 0.44 0.44 0.4 0.55 0.47 0.42 0	0.58 0 0 0 0 0.45 0.16 0.5 0.5	0 0 0 0 0 0.33 0.22 0.22	0.21 0.45 0.16 0.5 0.6 0.33 0.22 0.22	425 75 125 175 200 275 175 175
$\pi \cdot 1.12 \cdot 58 = 220$	{ 1.4 2.7 1.4	0 0 0	2 1.5 0	0 0 0	0.3 0 0	0.6 0.69 0.2	0.33 0.2 0.2	150 200 150
$\pi \cdot 0.75 \cdot 57 = 102$	{ 6 6 6 6 6 6 6 6 6	0 0 0 0 0 0 0 0 0	1 1 1 1 1 1 1 0.64	1 0.2 0 0 0 0 0 0	0 0 0.3 0.48 0.2 0.08 0 0	0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.4	75 125 125 250 150 250 150 150	0.4 1.1 1.1 0.84 1.03
$\pi \cdot 1.82 \cdot 10$	{ 6 6	0 0	0.64 1	0 0	0.26 0.08 0 0	0.13 0.13 0.7 0.06	0.250 0.250 0.250 0.250	53 53 53 70

With all the cation exchangers of the mixed (sulfonated coal, KU 1) and sulfonic acid (Espirat) types, replacement of hydrogen ions by ammonium ions is most rapid in an alkaline medium. It is interesting to note the reports by other authors [6] of slow replacement of hydrogen ions on weakly acidic resins, and retarded replacement on mixed exchangers; our results are in agreement with Walton's data [7]. The affinities of the ions for cation exchangers form the following series: $Mg^{++} > NH_4^+ > K^+ > Na^+$.

The Michaels method is applicable only when the ion removed from the solution has greater affinity for the ion exchanger than the ion bound in the resin; in our case we can find the dynamic characteristics for exchange of ammonium ions from carbonate - bicarbonate solution for sodium ions in the resin (formation of sodium carbonate - bicarbonate solution). The results of Experiment No. 4 (Table 1) show that the height of the exchange zone is 16.29 cm, and the zone velocity is 0.0026 cm/second. Regeneration of the ion exchanger, i.e., elution of ammonium ions from the resin, is more difficult; the height of the exchange zone is greater than the height of our column. This shows that spreading of the zone takes place in this instance, and dynamic data obtained in experiments on regeneration of the ion exchanger are of no value for calculation. The consumption of sodium chloride for regeneration should be greater than the consumption of ammonium carbonate - bicarbonate in exchange. Dynamic data on the adsorption of magnesium ions is quite interesting. The presence of sodium cations (common with the exchanger cations) in the solution sharply decreases the adsorption intensity, increases the height of the exchange zone, but does not prevent adsorption of these cations; the accumulation of magnesium in the resin does not exceed 15-20% of the total capacity of the cation exchanger; therefore presence of magnesium ions in the working liquors should not lead to complications in the exchange process.

Preparation of sodium carbonate and bicarbonate solutions. Dilute solutions are generally met in ion-exchange practice, and ion exchange in concentrated solutions has been studied very little. It seems likely that complete conversion would be difficult to achieve with the use of concentrated solutions; there can hardly be any question of the use of saturated sodium chloride solutions.

The conversion of brines from our salt lakes, without preliminary removal of magnesium ions, is worthy of consideration.

Data on ion exchange in these complex liquors on sulfonated coal in the sodium form are presented in Table 2.

The degree of conversion of ammonium carbonates into the corresponding sodium salts depends on many factors: the exchange of ammonium ions for sodium ions is hindered by increase of carbonate concentration in the influent liquor and with increase of the volumetric liquor rate; admixtures of sodium chloride have the same effect.

TABLE 3
Regeneration Data for the Ion-Exchange Column

Column volume 220 cc, liquid flow rate $\frac{VL}{V_{col/hr}} = 1.4$

Normality of influent		Normality of effluent		Volume of effluent (ml)	Amm. chloride yield (meq/g)	Conversion of sodium chloride (%)
NaCl	(NH ₄) ₂ CO ₃	NH ₄ Cl	(NH ₄) ₂ CO ₃			
2.0	0.1	0.84	0.18	150	1.15	42
2.0	0.1	0.62	0.3	200	1.3	31
1	0.1	0.49	0.14	200	1.16	49

It is possible to find conditions in which 1 meq of sodium carbonates is obtained per 1 g of sulfonated coal, and the conversion of ammonium into sodium salts can be raised to 70%, i.e., 1 N sodium bicarbonate solution can be obtained from 1.5 N ammonium bicarbonate solution. The solution can be boiled to remove unconverted ammonium carbonates; in some cases this process may be combined with utilization of the sodium carbonate liquors obtained; for example, in precipitation of magnesium from salt lake brines.

Regeneration data for the ion-exchange column are given in Table 3.

It is seen that the conversion of sodium chloride is somewhat lower than that of ammonium carbonate; the yields of ammonium chloride and sodium carbonate per gram of exchanger are approximately the same.

SUMMARY

As the result of the experiments described, a fairly simple method for production of sodium carbonate and bicarbonate solutions may be recommended: 1) utilization of natural common-salt brines of 5-10% concentration without careful removal of magnesium salts, and without increase of concentration by additional saturation; 2) if there is a shortage of fresh water, the entire production cycle can be run on brine; 3) the ammonia cycle follows the scheme of the soda industry; 4) sulfonated coal, as the most easily available and cheapest, should be used as the ion exchanger.

In conclusion, I thank L. A. Belogorskaya, M. F. Kovaleva, N. E. Khomenko, and V. I. Lukashenko for assistance in the experimental work.

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SORPTIONAL PROPERTIES OF CLAYS FROM THE ROMNY AND REVOKA REGIONS OF THE UKRAINIAN SSR

S. N. Kuz'menko and L. Ya. Kurilenko

Many clays are effective sorbents and are used for purification of liquids and sorption of vapors.

Among the best-known of our mineral sorbents are gumbrin, Zikeevo clay, etc. One of us [1] demonstrated the suitability of a clay of the tripoli type ("zelenka") from the Khar'kov region for regeneration of transformer and other oils. It was desirable in this connection to study the sorptional properties of certain other Ukrainian clays. Clays from the Romny and Revovka regions were investigated.

EXPERIMENTAL

To obtain comparable results, we used the same method as in the earlier study of the sorptional properties of Khar'kov clay of the tripoli type ("zelenka") [1].

Romny clay occurs in extensive deposits in the region of the Zolotukha mountain, Suma province, the Ukrainian SSR. It has been used for clay suspensions in oil-well drilling. Its color is pale yellow in the dry state, and slightly greenish when moist. It does not froth with HCl solution. A 5% aqueous suspension, made from clay ground down to pass through a sieve with 1600 holes/cm², is fairly stable even for 4 days, and exhibits whitish, opalescent turbidity; the pH of an aqueous extract, determined by the Michaelis colorimetric method, is 7.2. The density of the air-dry clay, determined pycnometrically, is 2.575. Another variety of this clay, known as "brecciated," is found in the same region [2].

Revovka clay. Considerable deposits of this clay are found near the village of Revovka, in the Kirovograd province of the Ukrainian SSR [3]. Samples from a pit made by the Kremenchug Geological Survey were taken for the investigation. This clay is extensively used for the industrial cooperative production of various ceramic wares. Its color is grayish white with a pinkish tinge in the dry state, and dark gray when moist. It does not froth with HCl solution. A 5% aqueous suspension (prepared as previously) is rather unstable, and becomes clear after 2 days as the result of complete sedimentation. The pH of an aqueous extract and density of the air-dry clay, determined as previously, are 7.1 and 2.455, respectively.

The results obtained in tests of these clays were compared with those for the sorbents studied previously—gumbrin [4, 5], Khar'kov clay of the tripoli type ("zelenka") [1, 6], and to some extent also for Chasov Yar clay (ch-1) [7].

The results of chemical and mechanical analyses of the clays are given in Tables 1 and 2.

The sorptional properties of clays usually vary for different substances [8], and therefore these clays were tested with vapors of aromatic hydrocarbons, aqueous solutions of organic dyes, and used mineral oils. The main purpose of the investigation was to determine the influence of the type of clay on its sorption capacity, and therefore the tests were performed with hydrocarbon vapors and dye solutions of constant concentrations.

Sorption of aromatic hydrocarbon vapors: C₆H₆, C₆H₅CH₃, and C₆H₄(CH₃)₂, was determined by the static (desiccator) method, from the weight increase of a sample of clay placed in a desiccator with the liquid hydrocarbon [9]. Chemically pure hydrocarbons were used. The determinations were performed at 20°. The clay was first ground to pass through a sieve with 1600 holes/cm².

The results of the experiments show that the sorptional properties of the other mineral sorbents — gumbrin, Khar'kov tripoli, and Chasov Yar clay (ch-1) — are better than those of Romny and Revovka clays.

TABLE 1
Results of Chemical Analyses of Clays (%)

Clay	Calci-nation loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Total
Romny	6.36	70.24	15.12	3.68	3.02	1.08	99.92
Revovka	7.34	67.18	22.30	2.10	0.84	0.97	100.73

TABLE 2
Results of Mechanical Analyses of Clays by the Sabanin Method

Clay	Cont. (%) of fractions with particle sizes (mm)				Total
	> 0.25	0.25–0.05	0.05–0.01	< 0.01	
Romny	1.90	27.06	17.04	54	100
Revovka	1.48	10.62	8.28	79.92	100

The sorption capacities of these materials for benzene and toluene vapors can be arranged in the following descending sequence: gumbrin, Chasov Yar clay (ch-1), Khar'kov "zelenka," Revovka and Romny clays. The absolute amounts sorbed are greater in the case of benzene than toluene for all five clays (Table 3).

TABLE 3
Sorption of Benzene and Toluene Vapors by Clays in 7.5 Hours

Sorbent	Weight increase (%) on initial weight	
	with C ₆ H ₆	with C ₆ H ₅ CH ₃
Clay:		
Romny	5	4.2
Revovka	6	4.8
Khar'kov "zelenka"	9	7.6
Chasov Yar clay	8.8	7.9
Gumbrin	12	10.1

However, the same does not hold for xylene vapor; in the case of Revovka clay the amount sorbed is less than that of toluene (3% rather than 5% in 7.5 hours), in the case of Romny clay it is more (5.2% rather than 4.2 in 7.5 hours), while gumbrin takes up roughly the same amounts of xylene and toluene in a given time.

The results show that Romny and Revovka clays have lower sorptional capacity than gumbrin for benzene, toluene, and xylene vapors, and also lower than Khar'kov tripoli and Chasov Yar clay (ch-1) for benzene and toluene. Revovka clay is somewhat superior to Romny clay in sorptional properties.

Sorption of organic dyes from aqueous solutions. The sorptional capacity of the clays was studied in relation to aqueous solutions of the following organic dyes: Malachite green, Methylene blue, and Basic fuchsin. The dyes were used as 0.05% solutions in distilled water. The clays were ground to pass through a sieve with 1600 holes/cm², and 1 g samples were shaken for 5 minutes with 100 cc of dye solution.

The liquids were left to settle for not less than 2 days, and the decolorization was then determined by means of the Dubosq colorimeter. The results are given in Table 4.

TABLE 4
Decolorization (%) of Aqueous Solutions of Organic Dyes by Clays

Sorbent	Dye		
	Malachite green	Methylene blue	Basic fuchsin
Clay:			
Romny	50	68	76
Revovka	95	95	96
Khar'kov "zelenka"	60	91	95
Gumbrin	95	93	95

It is seen that the clays differ in their sorptional capacities for organic dyes [10].

Revovka clay was found to have high sorptional capacity, somewhat higher than gumbrin, for all three dyes.

The sorption of all three dyes by Romny clay was relatively low.

Regeneration of used mineral oils. Used mineral oils—transformer and aviation (MS)—were tested.

The experiments with used transformer oil were performed under laboratory conditions, 15% of clay by weight being added to the oil.

The clay was first ground to pass a 1600 holes/cm² sieve and dried for 1 hour at 110–120°. The treatment was continued for 1 hour at 80°, followed by settling for 1 day and subsequent filtration; the constants of the regenerated oil were then determined.

The results of the experiments are given in Table 5.

TABLE 5
Regeneration of Used Transformer Oil by Clays

Oil and sorbent	Acid number (mg KOH per g oil)	Soda test	Reaction of aqueous extract	Color	Note
Oil by GOST No. 982-43	not over 0.05	not over 2 points		—	
Original oil	0.104	4		Red	
Clay:					
Romny	0.046	2	neutral	Golden red	Regenerated oil
Revovka	0.047	2		Golden red	
Khar'kov "zelenka"	0.037	1		Golden	
Gumbrin	0.030	1-2		Golden red	

It is clear from the results that Romny and Revovka clays are suitable for regeneration of used transformer oil. This is shown primarily by the changed color of the regenerated oil as compared with the original; its color changes after regeneration by these clays in the same way as after regeneration by gumbrin. In addition, oil regenerated by Romny and Revovka clay conforms to the GOST specification.

Used aviation oil (MS) was also regenerated under laboratory conditions by the contact method for 1 hour at 100-110°. Ten percent of each clay on the weight of oil was taken; the clay was previously ground to pass through a 1600 holes/cm² sieve and dried for 1 hour at 110-120°.

The aviation oil was almost free from gasoline fractions, so that distillation of these fractions was unnecessary.

The results of the experiments are given in Table 6.

TABLE 6
Regeneration of Used Aviation Oil (MS) by Clays

Oil and sorbent	Density	Water	Engler viscosity at 100°	Mechanical impurities	Acid number (mg KOH per g oil)	Conradson coke value (%)	Note
Oil by GOST No. 1013-41	Not over	absent	Not below	absent	Not over	Not over	
Original oil	0.895		2.9		0.07	0.3	
Clay:							
Romny	0.88	absent	2.8	0.03	0.6	0.3	
Revovka	0.89	absent	3.01	absent	0.05	0.20	
Khar'kov		"					
"zelenka"	0.89	"	3	"	0.03	0.28	Regenerated oil
Gumbrin	0.89	"	3.01	"	0.02	0.26	
			3.01	"	0.07	0.28	

The data are up to GOST specifications and show that Romny and Revovka clays are also suitable for regeneration of used aviation oil (MS). Favorable results can therefore be expected in tests of these clays under production conditions, and also in their use for regeneration of other used mineral oils. The sorptional properties of Romny and Revovka clays were roughly the same in this respect.

SUMMARY

1. Romny and Revovka clays are less effective sorbents for benzene, toluene, and xylene vapors than are gumbrin, Khar'kov tripoli ("zelenka"), or Chasov Yar (ch-1) clay.
2. Revovka clay is an effective sorbent for aqueous solutions of Malachite green, Methylene blue, and Basic fuchsine dyes; it is superior in nearly every respect to gumbrin and Khar'kov "zelenka".
3. Laboratory experiments on regeneration of used transformer and aviation (MS) mineral oils by means of Romny and Revovka clay by the contact method gave satisfactory results.
4. These laboratory experiments provide a basis for studies of regeneration of used mineral oils by means of Romny and Revovka clays.

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THE INTERACTION OF STANNOUS AND STANNIC OXIDES WITH STANNOUS SULFIDE

D. N. Klushin, O. V. Nadinskaya, and K. G. Bogatina

In the course of development of a technological process for extraction of tin from lean ores [1, 2] it became necessary to study reactions of stannous and stannic oxides with stannous sulfide, which are side reactions in the oxidation of stannous sulfide by atmospheric oxygen. The literature contains virtually no information on the subject.

EXPERIMENTAL

The apparatus shown in Fig. 1 was used for studies of the reactions of stannous sulfide (SnS) with stannous (SnO) and stannic (SnO_2) oxides.

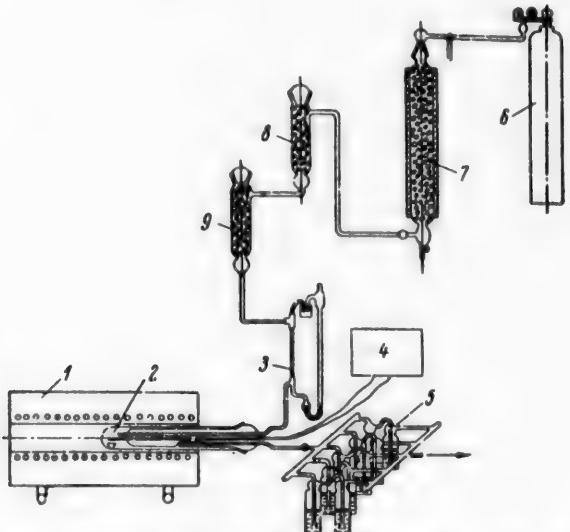


Fig. 1. Apparatus for studying reactions of $\text{SnO} + \text{SnS}$ and $\text{SnO}_2 + \text{SnS}$. 1) Furnace; 2) quartz tube; 3) micro-rheometer; 4) potentiometer; 5) absorption flasks; 6) nitrogen cylinder; 7) copper; 8) askarit; 9) P_2O_5 .

The experiments were performed in an atmosphere of purified nitrogen which was passed into the reaction tube; the nitrogen rate was kept constant at 500 cc/minute, and was checked by means of a microrheometer.

The nitrogen was freed from oxygen in a column made of molybdenum glass, heated externally (by a Nichrome heater) and filled with active copper [3] prepared by precipitation and reduction of copper from $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ on silica gel.

The copper was reduced by hydrogen at 200° until no more moisture was evolved. The column was likewise cooled in a stream of hydrogen. The oxygen content of the exit gas was tested colorimetrically at intervals by absorption in ammoniacal cuprous chloride [4]; moisture and carbon dioxide were removed from the nitrogen by means of askarit (asbestos impregnated with caustic potash and calcined) and phosphorus pentoxide.

The following experimental procedure was used: a weighed sample consisting of equimolecular amounts of SnO (or SnO₂) and SnS was put in an alundum boat, previously heated to constant weight and weighed. The boat was put in the quartz reaction tube. The free volume of the reaction tube was reduced to a minimum by means of a quartz plug placed in the tube. The reaction tube and absorption flasks were blown through with purified nitrogen before each experiment. When the temperature was 50° above the required value, the furnace was moved onto the reaction tube, and the instant at which the required temperature was reached was taken as the start of the experiment. The temperature was measured and maintained at the required level to within ± 5° by means of a platinum/platinum-rhodium thermocouple and an electronic potentiometer. The hot junction of the thermocouple was immediately above the boat with the sample.

The gases from the reaction tube passed through a distributing tube with stopcocks into absorption flasks containing a neutral 2% solution of hydrogen peroxide. To increase the surface and the time of contact of the gas with the absorbent solution, the bubbler tubes of the absorption flasks terminated in porous plates made from No. 1 Schott filters.

At the end of the experiment the furnace was moved away from the tube, and the boat containing the sample was cooled to room temperature in a stream of nitrogen. The boat with the cinder was removed from the tube and weighed, the cinder was removed, ground, and subjected to phase, chemical, x-ray structural, and mineralogical analyses. The following starting materials had to be prepared for the investigation: stannous sulfide, and stannous and stannic oxides.

Stannous sulfide was prepared as follows: pure metallic tin was melted in an alundum crucible under a layer of carbon. Sulfur, previously freed from arsenic and selenium, was added at 800° with vigorous stirring. The crucible was cooled and the top layer was separated off; this was crushed, mixed with sulfur, placed in an alundum crucible with a close-fitting graphite lid, and kept at 850° for 3 hours under a layer of carbon. Mineralogical and x-ray analysis of the product showed that it consisted only of tin monosulfide, and contained 78.1% tin and 21.8% sulfur.

The reagents used for preparation of stannous oxide (SnO) were stannous chloride, pure tin metal, and chemically pure ammonia solution. The preparation method was as follows: stannous chloride solution was boiled with tin metal to remove quadrivalent tin, and ammonia was added to precipitate stannous hydroxide. The mixture was then heated on a bath consisting of saturated sodium chloride solution. When heated, the white hydroxide darkened and was gradually converted into a heavy black microcrystalline precipitate of stannous oxide. It was washed thoroughly and dried at 100-105°.

It was shown by x-ray structural analysis that the product consisted of stannous oxide only; it contained 87.9% tin by chemical analysis.

Stannic oxide used was of analytical reagent grade, made by the Chemical Reagent Works. Chemical analysis showed it to contain 78.5% tin.

Study of the Reaction Between Stannous Oxide and Sulfide

Thermodynamic calculations for the reaction



Showed that the free-energy change in this reaction can be calculated from the equation

$$\Delta Z = 85416 + 10T \lg T - 3.6 \cdot 10^{-3}T^2 - 71T.$$

The values of the free-energy changes at different temperatures, calculated from this equation, are as follows:

T (in °C)	300	400	500	600	700	800	900	1000
ΔZ	59355	55035	50708	46364	41999	37606	33183	28723

It follows from these results that stannous oxide and sulfide cannot react with formation of tin and liberation of sulfur dioxide in the 300-1000° range.

The experiments were performed in the 550-1100° range, and were 30 minutes in duration.

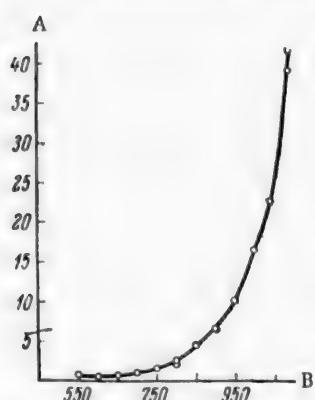


Fig. 2. Variations of cinder weight with temperature in the reaction of SnO with SnS .
A) Weight loss of cinder (% of original), B) temperature (in °C).

The samples, consisting of intimate mixtures of equimolecular amounts of stannous oxide and sulfide, each weighed 3.0 g. The results of the experiments are given in Tables 1-3 and plotted in Fig. 2.

The data in Tables 1-3 and Fig. 2 show that variations of the experimental temperature in the 550-1100° range result in changes in the sample weight; at 750-850° this change was 1.5-5.3%, and then increased very rapidly with temperature (Fig. 2), reaching 41.4% at 1100°.

Analysis of the sublimes showed that the weight loss is mainly due to volatilization (which begins at 750°) of stannous sulfide, and only to a very small extent to formation of sulfur dioxide. This latter component of the loss was not taken into account, as it was only 0.09% of the initial sulfur.

Observations showed that another condensation region appears at 900°, but it was so small that the sublimate could not be collected. The results of chemical phase analysis of the cinder are given in Table 2.

It is clear from Table 2 that there is no reaction between stannous sulfide and stannous oxide in the 550-1100° range. As Table 1 shows, the very slight evolution of sulfur dioxide in the 600-900° range may be ignored for practical purposes.

TABLE I
Variations of Sample Weight and Weight of the Collected Sublimate at Different Experimental Temperatures

Temp. (in °C)	Wt. of cinder (g)	Wt. loss (g)	Sublimate collected		Sulfur collected (% of original)
			in g	in %	
600	2.977	0.2	Nil	"	—
650	2.981	0.7	"	"	0.09
700	2.974	1.0			0.09
750	2.959	1.5	Sublimate formed the same	"	0.09
800	2.928	2.5	0.06	2.0	0.04
850	2.844	5.3	0.23	7.7	0.09
900	2.818	6.2	0.34	10.9	
950	2.705	10.0	0.43	14.3	
1000	2.504	16.6	0.805	26.8	
1050	2.332	22.4			
1100	1.759	41.4			

Table 2 shows that stannous sulfide remains unchanged in the temperature range studied, while stannous oxide forms metallic tin and higher tin oxides. Mineralogical and x-ray analysis showed that the cinder formed at 600° contains the monoxide, sesquioxide, stannous sulfide, and metallic tin.

In the 650-950° range stannous oxide was not detected either by mineralogical or by x-ray analysis, and the cinders mainly consisted of stannous sulfide and small amounts of metallic tin and its sesquioxide and dioxide.

Chemical phase analysis of the cinders obtained over the entire temperature range studied revealed the presence of certain amounts of stannous oxide. Since the decomposition reaction of stannous oxide may have been not quite complete, and since chemical analysis is more accurate than x-ray structural or mineralogical analyses for low contents, we accepted the results of chemical phase analysis given in Table 2.

TABLE 2
Phase Composition of Cinders

Temp. (in °C)	Composition of cinder							
	Sn _{met}		SnO		SnS		SnO ₂ , Sn ₂ O ₃	
in %	in g	in %	in g	in %	in g	in %	in g	
600	5.4	0.14	29.7	0.81	56.9	1.55	12.8	0.35
650	13.7	0.41	4.0	0.12	51.9	1.55	25.5	0.76
700	12.4	0.37	11.4	0.34	51.4	1.53	25.6	0.76
750	14.5	0.43	2.4	0.07	53.0	1.57	24.3	0.72
800	12.9	0.38	2.7	0.08	53.3	1.56	31.1	0.91
850	14.4	0.41	2.5	0.07	53.8	1.53	33.4	0.95
900	15.2	0.43	0.7	0.02	52.9	1.49	32.3	0.91
950	15.9	0.43	6.6	0.18	48.8	1.32	24.4	0.66
1000	17.2	0.43	2.8	0.07	48.7	1.22	28.3	0.71
1050	18.0	0.42	8.6	0.20	48.4	1.13	24.0	0.56
1100	19.3	0.32	13.1	0.23	42.6	0.75	21.6	0.38

Mineralogical analysis of the cinders formed at 950° and higher revealed the presence of a eutectic mixture consisting of stannous oxide and sulfide. However, the amount present was very small in comparison with stannous sulfide, stannic oxide, and metallic tin.

Since in this case metallic tin can be formed only by decomposition of stannous oxide, the mechanism of the decomposition reaction can be determined by calculation of the Sn_{met}:Sn_{SnO₂, Sn₂O₃} ratio in the cinder (Table 3).

TABLE 3
Behavior of Tin Compounds in the Reaction Between Stannous Sulfide and Oxide at Various Temperatures

Experimental temperature (in °C)	Tin reacted as		Tin formed as				Tin as SnS				Ratio in cinder Sn _{met}	
	SnO		Sn _{met}		SnO ₂ , Sn ₂ O ₃		remains in cinder		sublimes			
	in %	in g	in %	in g	in %	in g	in %	in g	in %	in g		
600	42.7	0.53	41.3	0.44	22.6	0.28	99.2	1.22	—	—	1 : 2	
650	91.9	1.14	33.4	0.41	48.4	0.6	99.2	1.22	—	—	1 : 4.4	
700	74.9	0.93	29.8	0.37	48.4	0.6	98.4	1.21	—	—	1 : 1.6	
750	94.3	1.17	34.7	0.43	45.9	0.57	100.6	1.24	Sublimate appeared	—	1 : 1.3	
800	93.5	1.16	30.6	0.38	58.4	0.72	100.0	1.23	The same	—	1 : 1.8	
850	94.3	1.17	33.4	0.41	60.5	0.75	98.4	1.21	Not collected	—	1 : 1.8	
900	98.3	1.22	34.7	0.43	58.4	0.72	95.9	1.18	4.4	0.05	1 : 1.6	
950	86.2	1.07	34.7	0.43	41.9	0.52	84.5	1.04	14.6	0.18	1 : 1.2	
1000	94.3	1.17	34.7	0.43	45.4	0.56	78.0	0.96	21.1	0.26	1 : 1.3	
1050	84.6	1.05	33.9	0.42	35.5	0.44	72.3	0.89	26.8	0.33	1 : 1.04	
1100	83.4	1.03	27.4	0.32	24.2	0.30	47.9	0.59	51.2	0.63	0.9 : 1	

It is seen in Table 3 that the ratio Sn_{met}:Sn_{SnO₂, Sn₂O₃} does not remain constant over the entire temperature range, but changes from 1:2 to 1:1. Consideration of these ratios leads to the conclusion that in the 600 to 950° range the predominant reaction is



In the 950-1100° range the predominant reaction is



It is known from the literature [5] that the behavior of SnO in an inert atmosphere can be divided into three temperature regions: 1) up to 400° solid SnO is unchanged, 2) in the 400-1040° range it decomposes relatively slowly by the reaction $4\text{SnO} \rightarrow \text{Sn} + \text{Sn}_2\text{O}_4$, 3) above 1040° SnO is stable in the liquid phase.

Decomposition of stannous oxide by the reaction



is improbable, as the ratio $\text{Sn}_{\text{met}} : \text{Sn}_{\text{SnO}_2}$ changes not from 1:3 as it should with this reaction mechanism, but from 1:2 to 1:1, as our results show.

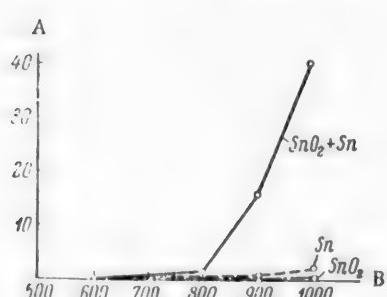


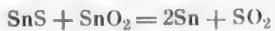
Fig. 3. Volatilization of tin and its oxides at various temperatures. A) Weight loss (%); B) temperature (in °C).

Klerding [6] used his experimental results to plot volatilization curves for metallic tin, stannic oxide, and a mixture of metallic tin and stannic oxide, in a vacuum at various temperatures (Fig. 3). These results show that the volatilization of tin from a mixture of metallic tin and stannic oxide, reaching 40% at 1000°, is very much greater than the volatilization of these substances when heated separately, which reaches 2-3% at 1000°.

It follows from the foregoing and from the data in Table 3 and Fig. 3 that starting from 900° stannous sulfide and oxide undergo partial sublimation; the decrease of the stannic oxide content of the cinder at 1000-1100° can be attributed to stability of stannous oxide at these temperatures.

Study of the Reaction Between Stannic Oxide and Sulfide

The free-energy change in the reaction



was calculated from the equation

$$\Delta Z = 89781 + 18.6T \lg T - 3.6 \cdot 10^{-3}T^2 - \frac{1.87 \cdot 10^5}{T} - 102T.$$

The free-energy changes calculated for different temperatures from this equation are given below:

T (in °C)	300	400	500	600	700	800	900	1000
ΔZ	59222	54627	50133	45530	40946	36500	31884	27406

It follows from these data that stannous sulfide cannot react with stannic oxide with liberation of sulfur dioxide.

The experiments were 30 minutes in duration, and were performed at 750, 800, 850, 900, 950, 1000, 1050, and 1100° in a nitrogen atmosphere. The nitrogen rate was 500 cc/minute. The samples consisted of an equimolecular mixture of stannic oxide and stannous sulfide. The sample weight was 3.0 g. The results of the experiments are given in Tables 4 and 5 and Figs. 4 and 5.

Consideration of the data in Table 4 and Fig. 4 shows that when a mixture consisting of 1.5 g of stannic oxide and 1.5 g of stannous sulfide is heated its weight loss rises from 1.7% at 750° to 38.3% at 1100°.

The weight loss is due to volatilization of stannous sulfide and formation and volatilization of sulfur dioxide. The sample can also lose weight by the reaction



in which, according to the data [6], (Fig. 3), the stannous oxide formed sublimes fairly easily. The presence of certain amounts of stannous oxide in the cinders, shown in Table 5, indicates that this reaction may take place.

TABLE 4
Changes in the Weight and Phase Composition of Cinders at Various Temperatures

Temperature (in °C)	Wt. of cinder (g)	Weight loss			Composition of cinder								Deviation (%)	
		in g		in %	% collected (of original)		Sn _{met}		SnO		SnS			
		in %	in g	in %	in %	in g	in %	in g	in %	in g	in %	in g		
750	2.95	0.05	1.7	0.09	4.3	0.04	0.3	0.01	43.4	1.28	46.8	1.38	-8.2	
800	2.93	0.07	2.3	0.19	2.0	0.06	0.40	0.011	44.7	1.31	44.7	1.31	-8.2	
850	2.86	0.14	4.7	0.1	4.9	0.14	0.8	0.023	45.8	1.31	44.0	1.26	-4.5	
900	2.73	0.27	9.0	0.14	4.0	0.11	0.8	0.023	43.9	1.20	46.1	1.26	-5.2	
950	2.56	0.44	14.7	—	7.0	0.18	0.4	0.011	42.9	1.10	44.5	1.14	-5.2	
1000	2.84	0.16	5.3	0.1	5.3	0.15	0.8	0.023	41.5	1.18	46.4	1.31	-6.3	
1050	2.68	0.32	10.7	0.35	6.7	0.18	1.3	0.034	42.9	1.15	47.0	1.26	-2.1	
1100	1.85	1.15	38.3	1.2	—	—	—	—	—	—	—	—	—	

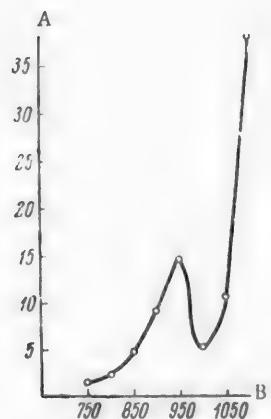


Fig. 4. Variations of cinder weight with temperature. A) Weight loss of cinder (% of original); B) temperature (in °C).

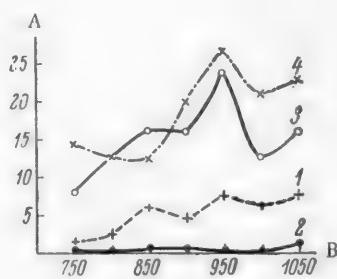


Fig. 5. Effects of temperature on the formation of Sn_{met} and SnO, and on the decomposition and volatilization of SnO₂ and SnS.
A) Formation of Sn_{met} (1), SnO (2), decomposition and volatilization of SnO₂ (3), SnS (4) (in %);
B) temperature (in °C).

The formation of metallic tin and sulfur dioxide, although in small amounts, indicates that the following reaction takes place:



The extent of this reaction may be estimated both from the amounts of metallic tin and sulfur dioxide formed, and from the amount of stannic oxide converted. The loss of stannous sulfide is not a measure of this reaction, as a definite proportion of it sublimes at the experimental temperatures used.

The large discrepancies between the amount of metallic tin formed (from 1.7 to 7.6%) and the loss of stannic oxide (from 8 to 16%) and stannous sulfide (from 11.9 to 22.2%) indicate that in addition to the reaction



there are other sources of loss of stannic oxide and stannous sulfide. It is most likely that stannous sulfide is lost by sublimation; it was shown earlier that the volatilization of stannous sulfide at these temperatures is considerable. According to the literature [6], stannic oxide and metallic tin are expended in the reaction



At higher temperatures stannous oxide and sulfide form a eutectic which is very pronounced at 1000°.

TABLE 5

Behavior of Tin Compounds in the Reaction Between SnS and SnO₂ at Various Temperatures

temp. (in °C)	Reacted				Formed			
	SnO ₂		SnS		Sn _{met}		SnO	
	in %	in g	in %	in g	in %	in g	in %	in g
750	8.0	0.12	14.7	0.22	1.7	0.04	0.4	0.009
800	12.6	0.19	12.6	0.19	2.5	0.06	0.4	0.01
850	16.0	0.24	12.6	0.19	5.9	0.14	0.8	0.02
900	16.0	0.24	20.0	0.30	4.7	0.11	0.8	0.02
950	24.0	0.36	26.7	0.40	7.6	0.18	0.4	0.01
1000	12.6	0.19	21.3	0.32	6.4	0.15	0.8	0.02
1050	16.0	0.24	23.3	0.35	7.6	0.18	1.3	0.03

SUMMARY

- There is no reaction between stannous sulfide and oxide in an inert atmosphere in the 600-1100° range.
- Stannous oxide decomposes in a nitrogen atmosphere in the 600-1100° range; contrary to certain literature data, at 600-950° it decomposes mainly by the reaction $3\text{SnO} \rightarrow \text{Sn} + \text{Sn}_2\text{O}_3$, and at 950-1100°, predominantly by the reaction $2\text{SnO} \rightarrow \text{Sn} + \text{SnO}_2$.
- There is virtually no reaction between stannous sulfide and stannic oxide in the 750-1100° range.
- There is a possibility of the reaction $\text{SnO}_2 + \text{Sn} \rightarrow 2\text{SnO}$ taking place; this accounts for the weight loss of the samples and decrease of the stannic oxide content in the cinder, and also for the discrepancy between the amount of metallic tin remaining in the cinder and the amount of stannic oxide converted.
- Stannous oxide and sulfide form a eutectic at temperatures of 950° and over.

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INHIBITION OF THE THERMAL DECOMPOSITION OF AMMONIUM NITRATE

B. Yu. Rozman and L. I. Borodkina

Veley [1] studied the kinetics of thermal decomposition of ammonium nitrate and found that the decomposition can be very much retarded by addition of ammonia to the nitrate during heating. Veley's results have been repeatedly confirmed by others who studied the thermal decomposition of ammonium nitrate. As the result of studies of the thermal stability of ammonium nitrate, definite types of compounds were found [1] which inhibit the thermal decomposition both of the nitrate and of the system nitrate-organic component. Such systems can be stabilized by compounds which liberate ammonia by reaction with the nitrate, and/or which combine directly with the nitric acid and nitrogen dioxide formed during decomposition. This class of compounds includes many metal oxides, carbonates (mainly of magnesium and of the alkaline earths), and urea, urotropine, and similar substances with high reactivity toward nitrogen oxide. Experimental results [2] show that urea and urotropine are very effective inhibitors of nitrate decomposition, being far superior to all the other substances tested.

The purpose of the present investigation was to obtain more detailed information on the inhibiting action of urea in the thermal decomposition of ammonium nitrate.

Two principal methods were used for evaluation of the inhibition effect: 1) the thermogravimetric method, consisting of periodic determinations of weight losses of test samples at a definite temperature, and 2) the manometric method. In addition, the pH of the nitrate before and after heating was determined in a number of cases.

TABLE 1
Effect of Urea Content of Ammonium Nitrate on Thermal Stability (Gravimetric Method)

Temp. (in °C)	Urea content (%)	Weight loss (%) after time (hours)								
		1/3	2 3	1	2	4	6	8	10	12
175	0	—	—	—	0.20	0.40	0.62	0.85	1.04	1.26
	0.10	—	—	—	0.18	0.33	0.48	0.58	0.70	0.80
	0.25	—	—	—	0.20	0.33	0.46	0.56	0.65	0.76
	1.00	—	—	—	0.17	0.30	0.43	0.52	0.62	0.60
200	0	—	—	0.52	1.35	2.80	4.00	5.32	6.40	7.30
	0.10	—	—	0.22	0.39	0.82	2.12	3.44	4.53	6.20
	0.25	—	—	0.22	0.52	0.85	1.30	2.27	3.54	4.25
	1.00	—	—	0.24	0.50	1.00	1.30	2.09	2.58	—
225	0	1.0	2.8	4.0	8.4	18.5	25.2	—	—	—
	0.10	0.4	0.7	1.4	5.8	15.5	24.5	—	—	—
	0.25	—	—	1.2	2.3	12.5	20.0	—	—	—
	1.00	0.4	0.7	1.0	1.6	5.5	13.1	—	—	—

The thermogravimetric experiments were performed with 10 g samples at 175, 200, and 225°. The manometric tests were carried out at 200 and 225° with samples weighing from 0.1 to 5 g. Manometric tests were not performed at 175° because of the very low decomposition pressure. The manometric tests were carried out without preliminary evacuation. To eliminate the influence of thermal expansion of air on the manometer readings, the manometer was connected only after the samples had been heated for 10 minutes.

The inhibitor (urea) contents of the test samples were varied from 0.01 to 1%. Since the best results are obtained with 0.1 to 1% of urea, most of the experiments were performed with samples of this composition.

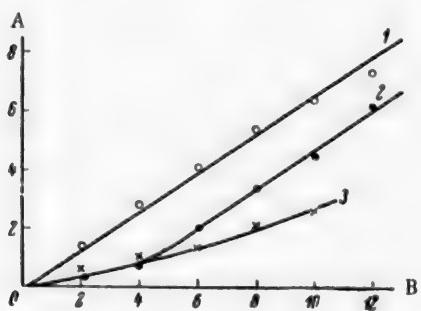


Fig. 1. Weight loss at 200°. A) Weight loss (%); B) time (hours); urea contents (%): 1) 0, 2) 0.1, 3) 1.0.

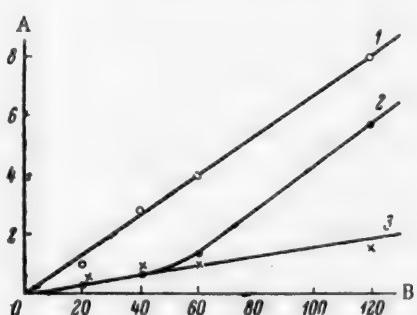


Fig. 2. Weight loss at 225°. A) Weight loss (%); B) time (minutes); urea content (%): 1) 0, 2) 0.1, 3) 1.0.

The results of some determinations of thermal stability by the thermogravimetric method are given in Table 1. Some of the results are presented in graphical form in Figs. 1 and 2.

The results of some monometric determinations of thermal stability at 200 and 225° (1 g samples) are given in Fig. 3.

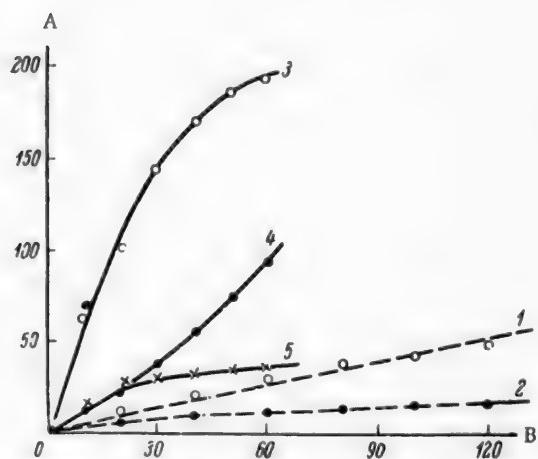


Fig. 3. Variation of decomposition pressure with time. A) Pressure (mm Hg); B) time (minutes); temperature (°C) and urea content (%): 1) 200 and 0, 2) 200 and 0.1, 3) 225 and 0, 4) 225 and 0.1, 5) 225 and 1.

in thermal stability. It follows that urea may be added to ammonium nitrate solutions before evaporation.

For accurate determination of the degree of inhibition with very small amounts of urea in the nitrate (from 0.01 to 0.05%), manometric tests were performed at 200°. It was found that an inhibition effect can be detected with only 0.02% urea present, although it is not large. At 0.03% urea content the results differ only a little from those obtained with 0.1% urea.

Very interesting results were obtained in determinations of the pH of inhibited nitrate after it had been heated for 1 hour at 200° and 0.5 hour at 225°. The pH of 10% aqueous solutions was determined. The pH of

The results obtained by both methods show that urea is an effective inhibitor of the thermal decomposition of ammonium nitrate. The inhibiting effect obviously decreases with time owing to decomposition of urea. Nevertheless, the life of the inhibitor is very considerable. At 200° a difference between the effects of 0.1 and 1% of urea only begins to appear 4 hours after the start of decomposition (Fig. 1). It is only at the end of this period that the decomposition rate of ammonium nitrate containing 0.1% of urea becomes equal to the decomposition rate of the pure nitrate. At 225° the difference appears considerably earlier, in less than one hour (Figs. 2 and 3).

Special experiments were carried out in which urea was added not to the dry nitrate but to 60-70% aqueous solutions, i.e., to solutions of the concentration obtained by neutralization. The solutions were then evaporated to dryness and the inhibited nitrate was tested by both methods simultaneously with nitrate inhibited by addition of urea to the dry salt rather than to the solution. Tests on samples inhibited in these different ways did not reveal any significant differences

an aqueous solution of nitrate which had not been heated was 5.0. Addition of 0.1-1% of urea to the nitrate produces little change in pH, which is then 5.15 on the average. However, as Table 2 shows, after heating the pH of inhibited nitrate is much higher than that of nitrate without inhibitor.

TABLE 2
Variations of pH of Ammonium Nitrate
After Heating

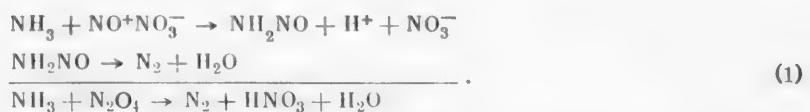
Urea content (%)	pH at temperature (in ° C)	
	200	225
0	3.15	2.9
0.01	3.4	—
0.02	3.8	—
0.03	4.7	3.0
0.05	4.9	3.1
0.10	5.75	5.5
1.0	6.55	6.6

The inhibition effect, as indicated by difference of pH, is noticeable even with 0.01% urea, although it is slight. From 0.03% (at 200°) the inhibition effect becomes considerable.

Thus, the results obtained by the two methods are generally in agreement. Therefore, it may be assumed that with 0.03-0.10% of urea in the nitrate an adequate degree of inhibition can be obtained under production conditions. The inhibiting mechanism of urea can be attributed to two causes.

1. Urea decomposes when heated, with liberation of ammonia. The extent of decomposition, and therefore of ammonia liberation, increases with rise of temperature. The liberated ammonia neutralizes the nitric acid formed by dissociation of the nitrate, and also removes nitrogen dioxide. Nitrogen dioxide is formed by thermal decomposition of nitric acid. Removal of nitrogen dioxide

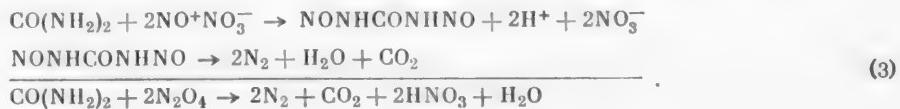
is most important, because it catalyzes the decomposition of ammonium nitrate [2]. The reaction between nitrogen dioxide and ammonia can be represented by the equation



2. In addition, nitrogen dioxide may react directly with urea, with liberation of nitrogen and carbon dioxide. This reaction is usually represented as



However, we consider that it is more correct to interpret the mechanism of this reaction in terms of a nitrosonium scheme [similarly to Eq. (1)]:



It has been shown [2] that, in addition to urea, urotropine is an effective inhibitor of thermal decomposition of ammonium nitrate. Its inhibition mechanism is similar to that of urea, because urotropine decomposes when heating with liberation of ammonia, and at 180-190° it evolves dimethylamine and trimethylamine [3]. Furthermore, urotropine itself reacts directly with nitrogen dioxide.

It is known that urea is thermally unstable. It is much less stable to heat than ammonium nitrate, as it begins to decompose even at 130°. The high thermal stability which we found for urea dissolved in ammonium nitrate solution is therefore unexpected.

Studies of the thermal stability in the system ammonium nitrate - urea revealed a most interesting mutual stabilization effect. Not only does urea, an inhibitor of nitrate decomposition, stabilize the nitrate, but conversely, ammonium nitrate stabilizes urea. The degree of stabilization of urea increases with the nitrate content of the system. The mechanism of this stabilization is not yet quite clear.

Urea has considerable thermal stability only in presence of a large excess of ammonium nitrate in the system. Because of this, increase of the urea content in the system from 1-2 to 5% leads to a decrease rather than an increase in the thermal stability of the system, because of intensified decomposition of the urea itself. It follows

that it is inadvisable to increase the inhibitor content of the nitrate above 1%, not only on economic grounds, but on considerations of thermal stability.

SUMMARY

Investigations of the thermal stability of ammonium nitrate with additions of urea showed that as little as 0.03-0.10% of urea in the nitrate acts as an effective inhibitor of the thermal decomposition of ammonium nitrate.

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STUDY OF THE RATES OF CERTAIN REACTIONS IN AQUEOUS SOLUTIONS CONTAINING CHLORINE DIOXIDE, CHLORINE, AND HYPOCHLOROUS ACID

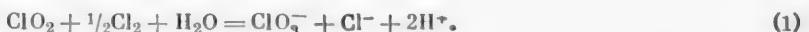
I. E. Flis, K. P. Mishchenko, and K. Yu. Salnis

The Leningrad Technological Institute

Chlorine dioxide made under industrial conditions always contains some chlorine as an impurity [1, 2]. As a result, aqueous ClO_2 solutions used in the pulp, paper, textile, and other industries contain chlorine and its hydrolysis products—hypochlorous and hydrochloric acids [3, 4]. In such solutions reactions of chlorine dioxide with chlorine and HClO are most likely. The rates and mechanism of these processes have been studied very little, despite the fact that they are important not only in relation to the practical use of chlorine dioxide, but also to more detailed studies of the properties of chlorine and its oxygen compounds.

This paper contains the results of calculations of rate constants of the reaction between chlorine dioxide and chlorine in aqueous solution at 10, 25, 35, 50, and 60°, and also experimental results obtained in a study of the reaction kinetics of chlorine dioxide and hypochlorous acid in weakly acidic solution ($\text{pH} = 5.5\text{--}5.7$) at 25, 35, and 50°.

Rate Constants of the Reaction



It is known that when chlorates are reduced by chlorides in an acid medium, a mixture of chlorine dioxide and chlorine is formed, and the following equilibrium is established [5-8]:



It has also been shown that when chlorine dioxide reacts with chlorine, chlorate and chloride are formed, with acidification of the solution [5, 9]. This leads to the conclusion that the reaction between ClO_2 and Cl_2 in accordance with Eq. (1) is very probable. This is also confirmed by the fact that Reaction (1) is accompanied by a decrease in the free energy of the system:

$$\Delta Z_{(1) 298^\circ}^0 = -2 \frac{\text{kcal}}{\text{mole}}.$$

The rate constants of this reaction can be calculated if the equilibrium constants and the rate constants for the reversible Reaction (1a) are known. The former were determined experimentally at 10, 25, 35, 50, and 60° by us, and the latter by Bray [5].

The calculations were based on the known relationship between the rate constants of a reversible reaction and its equilibrium constant:

$$K_1 = \frac{K_{1a}}{K},$$

where K_1 and K_{1a}^* are the rate constants of Reactions (1) and (1a), and K is the equilibrium constant of Reaction (1a). Values of K , K_1 , and K_{1a} are given in Table 1.

TABLE 1
Rate Constants of Reactions (1a) and (1) and Equilibrium Constants of Reaction (1a) at Various Temperatures

t °C	10	25	35	50	60
K_{1a}	$0.4 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$3.3 \cdot 10^{-5}$	$10.0 \cdot 10^{-5}$	$19.5 \cdot 10^{-5}$
K	$3.8 \cdot 10^{-2}$	$9.3 \cdot 10^{-2}$	$11.0 \cdot 10^{-2}$	$8.5 \cdot 10^{-2}$	$7.3 \cdot 10^{-2}$
K_1	$1.1 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$11.7 \cdot 10^{-4}$	$26.7 \cdot 10^{-4}$

The method of least squares was used to find the following equation for K_1 as a function of temperature:

$$K_1 = 0.1093147 - 0.0007538T + 0.0513T^2.$$

The calculated values of K_1 were used for a series of calculations of the rate of Reaction (1) for different absolute and relative contents of ClO_2 and Cl_2 , and different temperatures.

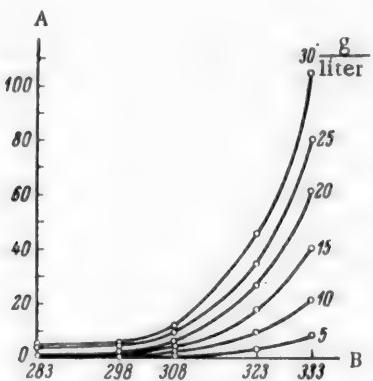


Fig. 1. Effect of temperature on the initial reaction rate of chlorine dioxide and chlorine with different concentrations of total active chlorine in solution: the solution contained 80% ClO_2 and 20% Cl_2 , expressed in oxidation equivalents; A) rate $v \cdot 10^6$ (moles/minute), B) temperature (in °C).

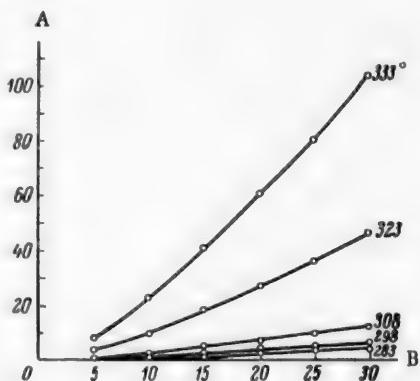


Fig. 2. Effect of total active-chlorine concentration on the reaction rate of chlorine dioxide and chlorine at various temperatures: the solution contained 80% ClO_2 and 20% Cl_2 , expressed in oxidation equivalents; A) rate $v \cdot 10^6$ (moles/minute), B) active-chlorine concentration (g/liter).

Figures 1 and 2 contain results for bleach liquors made by the method developed in the Leningrad Technological Institute, and containing 80% ClO_2 and 20% Cl_2 (in oxidation equivalents). The following main conclusions may be drawn from the course and configuration of the curves and from the data in Table 1: increase of temperature from 10 to 60° results in an appreciable increase of the rate of Reaction (1), the rate constant increasing approximately 25-fold; the higher the content of active chlorine in the solution, the greater is the increase of the reaction rate at a given temperature.

* The values of K_{1a} at 10, 25, 35, 50, and 60° were found by graphical interpolation from Bray's experimental data [5].

Decomposition Rate of Chlorine Dioxide and Hypochlorous Acid Present Together in Aqueous Solution

Förster and Dolch [10] studied reactions in solutions of chlorine dioxide and hypochlorite, and concluded that hypochlorous acid does not react with chlorine dioxide. This result was not confirmed by later work [9, 11]. It was shown experimentally that the reaction of ClO_2 with HClO is accompanied by formation of chlorates and chlorides and acidification of the solution. However, there is as yet no experimental basis to account for the kinetics and mechanism of the reactions taking place. We studied the rate of decomposition of chlorine dioxide and hypochlorous acid at 25, 35, and 50°.

Gaseous chlorine dioxide was prepared by reduction of potassium chlorate with oxalic acid in presence of sulfuric acid:



The chlorine dioxide was first liquefied to remove carbon dioxide and any possible chlorine impurities. The original solutions were prepared by evaporation of the liquid ClO_2 and absorption in distilled water.

Hypochlorite solution was prepared by chlorination of caustic soda solution free from carbonate. Before the experiments a calculated amount of hydrochloric acid was added to the hypochlorite solution to give pH 5.5-5.8. Under these conditions the solution contains almost entirely hypochlorous acid [12, 13]. A certain amount of a buffer mixture consisting of mono- and di-substituted phosphates was added to this solution to ensure constant pH during the experiment, followed by a definite amount of chlorine dioxide solution. All the solutions used were heated to the required temperature before the start of the experiments. The initial concentrations of the solutions were determined precisely before they were mixed. After definite time intervals samples were taken and analyzed for ClO_2 and HClO . For this, in one accurately measured volume of each sample the total contents of chlorine dioxide and hypochlorous acid were determined by the usual iodometric method, and to another measured volume a definite amount of alkaline hydrogen peroxide solution was added. The following reactions took place:

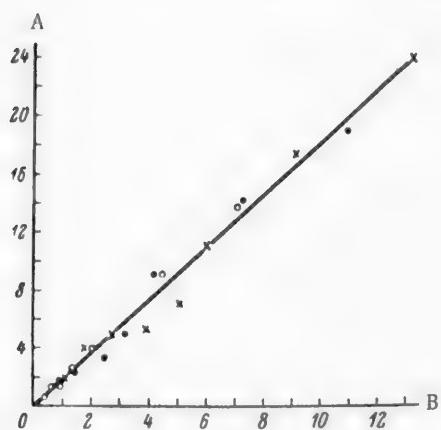


Fig. 3. Calculation of the rate constant of the reaction of chlorine dioxide with hypochlorous acid at 35°; A) values of $\frac{dC_{\text{HClO}}}{dt} \cdot 10^4$, B) values of $C_{\text{ClO}_2} \cdot C_{\text{HClO}} \cdot 10^4$.

method. The analytical data were used to calculate the ClO_2 and HClO contents of the sample. The results of these experiments are given in Table 2.

It follows from the results that, regardless of temperature, the number of moles of chlorine dioxide reacted is greater than that of hypochlorous acid at all the concentration ratios studied.

The rate of reaction of chlorine dioxide with hypochlorous acid may be represented by the equation

$$-\frac{dC_{\text{HClO}}}{dt} = K_2 \cdot C_{\text{ClO}_2}^x \cdot C_{\text{HClO}}^y. \quad (5)$$

TABLE 2

Results of Determinations of the Decomposition Rate of Chlorine Dioxide and Hypochlorous Acid in Solution at 25, 35, and 50°

Time (min)	Change of ClO_2 con- centration (M)	Change of HClO con- centration (M)	$\frac{\Delta C_{\text{ClO}_2}}{\Delta C_{\text{HClO}}}$	Notes
25°				
10	0.0162	0.0120	1.35	
20	0.0222	0.0130	1.70	
30	0.0257	0.0168	1.53	
60	0.0292	0.0185	1.57	
90	0.0317	0.0190	1.67	
150	0.0330	0.0191	1.70	
10	0.0132	0.0093	1.42	
20	0.0192	0.0103	1.86	
30	0.0232	0.0108	2.15	
45	0.0247	0.0113	2.18	
60	0.0282	0.0135	2.09	
10	0.0180	0.0125	1.44	
20	0.0220	0.0140	1.57	
30	0.0250	0.0150	1.67	
45	0.0261	0.0155	1.69	Initial concentration of HClO 0.0520 M
35°				
10	0.0336	0.0205	1.64	
20	0.0384	0.0220	1.75	
30	0.0404	0.0251	1.61	
40	0.0414	0.0255	1.62	Initial concentration of HClO 0.0535 M
15	0.0350	0.0255	1.37	
20	0.0360	0.0270	1.33	
25	0.0390	0.0280	1.40	
40	0.0398	0.0289	1.38	Initial concentration of HClO 0.0320 M
5	0.0282	0.0190	1.48	
10	0.0312	0.0215	1.45	
15	0.0327	0.0238	1.37	
20	0.0342	0.0240	1.43	
25	0.0347	0.0288	1.20	
40	0.0353	0.0297	1.18	
50°				
10	0.0350	0.0226	1.55	
20	0.0381	0.0197	1.93	
30	0.0384	0.0226	1.70	
45	0.0388	0.0231	1.68	
60	0.0394	0.0235	1.67	Initial concentration of HClO 0.0350 M

The experimental data were first used for determination of $\frac{dC_{\text{HClO}}}{dt}$. These values were found by graphical differentiation. Values of x and y corresponding to constant K_2 were found next. It was thereby found that a linear relationship between $\frac{dC_{\text{HClO}}}{dt}$ and $(C_{\text{ClO}_2}^x \cdot C_{\text{HClO}}^y)$ is obtained with $x = 1$ and $y = 1$. Figure 1 shows this relationship for 35°. Similar results were obtained for 25 and 50°. Table 3 contains values of the rate constant K_2 calculated from Eq. (5) for $x = 1$ and $y = 1$, and other kinetic data characterizing the reaction of chlorine dioxide and hypochlorous acid.*

The average values of the rate constant K_2 calculated from all the experimental data for 25, 35, and 50°, are 1.28 ± 0.93 , 1.82 ± 0.02 , and 4.58 ± 0.05 , respectively.

TABLE 3
Kinetic Data for Decomposition of HClO
in Solution in Presence of ClO₂

HClO concentration (M)	$-\frac{dC_{\text{HClO}}}{dt}$	$C_{\text{HClO}} \cdot C_{\text{ClO}_2}$	K_2
------------------------	--------------------------------	--	-------

25°

0.0325	0.00126	0.00110	1.27
0.0305	0.00110	0.00088	1.28
0.0290	0.00095	0.00076	1.36
0.0270	0.00085	0.00064	1.40
0.0255	0.00070	0.00052	1.28
0.0220	0.00050	0.00041	1.29

35°

0.0450	0.00370	0.00157	1.86
0.0400	0.00190	0.00110	1.80
0.0365	0.00140	0.00073	1.92
0.0340	0.00090	0.00042	2.14
0.0330	0.00050	0.00032	1.50
0.0320	0.00035	0.00025	1.60
0.0315	0.00024	0.00014	1.70
0.0284	0.00017	0.00009	1.84

50°

0.0290	0.00300	0.00085	4.35
0.0263	0.00260	0.00062	4.19
0.0240	0.00200	0.00045	4.44
0.0225	0.00130	0.00028	4.64
0.0190	0.00095	0.00020	4.70
0.0175	0.00070	0.00015	4.66
0.0152	0.00038	0.00004	4.50

TABLE 4
Kinetic Data for Decomposition of Chlorine Dioxide in Aqueous Solution in Presence of HClO

ClO ₂ concentration (M)	$-\frac{dC_{\text{ClO}_2}}{dt}$	K'_3	K_3
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25°

0.0312	0.0027	0.76	0.023
0.0290	0.0018	0.83	0.024
0.0262	0.0015	0.80	0.021
0.0237	0.0014	0.98	0.023
0.0210	0.0012	1.14	0.024
0.0185	0.0009	1.17	0.020

35°

0.0350	0.00500	1.68	0.057
0.0275	0.00350	2.10	0.058
0.0200	0.00280	3.50	0.070
0.0125	0.00200	6.90	0.088
0.0100	0.00100	5.10	0.051
0.0079	0.00080	7.50	0.050
0.0050	0.00036	8.00	0.030
0.0032	0.00011		

50°

0.0293	0.0063	3.10	0.088
0.0235	0.0049	2.37	0.093
0.0190	0.0035	4.10	0.079
0.0127	0.0023	6.20	0.095
0.0105	0.0019	10.00	0.092
0.0087	0.0015	11.40	0.084
0.0050	0.0008	14.00	0.076
0.0042	0.0005	12.00	0.070

It follows from these results that the rate of reaction of chlorine dioxide and hypochlorous acid is satisfactorily represented by the equation

$$-\frac{dC_{\text{HClO}}}{dt} = K_2 \cdot C_{\text{ClO}_2} \cdot C_{\text{HClO}}. \quad (6)$$

However, the decomposition rate of chlorine dioxide cannot be represented by Eq. (6) only, and it is reasonable to suppose that it is necessary to introduce a further term into the kinetic equation for this purpose:

* Table 3 contains only a part of the values calculated from the experimental data.

$$-\frac{dC_{\text{ClO}_2}}{dt} = K_2 \cdot C_{\text{ClO}_2} \cdot C_{\text{HClO}} + K_3 \cdot C_{\text{ClO}_2}^z. \quad (7)$$

The value of $-\frac{dC_{\text{ClO}_2}}{dt}$ was also determined from experimental data by graphical differentiation.

Using Eq. (7) to calculate z , we found that K_3 is satisfactorily constant when $z = 1$.

Table 4 contains some of our values for $\frac{dC_{\text{ClO}_2}}{dt}$ at various ClO_2 concentrations and different temperatures.

Values of K_3 and K_3^z , calculated from Eq. (7) with z taken as 1 and 2, respectively, are also given.

The average values of K_3 calculated from all the experimental data at 25, 35, and 50° are 0.022 ± 0.001 , 0.055 ± 0.001 , and 0.087 ± 0.002 , respectively.

Decomposition Mechanism of Chlorine Dioxide in Aqueous Solutions in Presence of Hypochlorous Acid ($\text{pH} = 5.5-5.7$)

It follows from the experimental data detailed above that the decomposition rate of chlorine dioxide in the solutions studied can be represented by the equation

$$-\frac{dC_{\text{ClO}_2}}{dt} = K_2 \cdot C_{\text{ClO}_2} \cdot C_{\text{HClO}} + K_3 \cdot C_{\text{ClO}_2}. \quad (7a)$$

Thus, apart from the main reaction between ClO_2 and HClO , there is another, the rate of which is proportional to the first power of the ClO_2 concentration. It seems likely that this reaction can be represented by the equation



In our experimental conditions, the chlorine formed is hydrolyzed rapidly and almost completely to form definite amounts of HClO :



With regard to the reaction of chlorine dioxide and hypochlorous acid, our experimental results show that its kinetics is determined by a reaction in which one mole of ClO_2 reacts with one mole of HClO . HClO probably oxidizes ClO_2 to chlorate in the process.

This reaction may be represented by the equation



but under our conditions chlorine is rapidly hydrolyzed



and the aggregate reaction between ClO_2 and HClO is then represented by the equation



The foregoing hypothesis for the decomposition mechanism of chlorine dioxide and its reaction with hypochlorous acid is consistent with the experimental data, according to which in these reactions the ratio $\frac{\Delta C_{\text{ClO}_2}}{\Delta C_{\text{HClO}}} > 1$. It is also in harmony with the fact that the final products in solution are chlorate and chloride.

SUMMARY

1. Chlorine dioxide may react with hypochlorous acid. The kinetics of the reaction can be represented by the equation

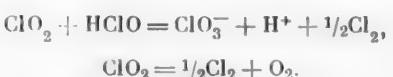
$$-\frac{dC_{\text{HClO}}}{dt} = K_2 \cdot C_{\text{ClO}_2} \cdot C_{\text{HClO}}.$$

The rate constant K_2 has the following values at 25, 35, and 50° respectively: 1.28 ± 0.03 , 1.82 ± 0.02 , and 4.58 ± 0.05 .

2. In weakly acidic media ($\text{pH} \approx 5.5-5.7$) in solutions containing chlorine dioxide and hypochlorous acid the kinetics of ClO_2 decomposition may be represented by the equation

$$-\frac{dC_{\text{ClO}_2}}{dt} = K_2 \cdot C_{\text{ClO}_2} \cdot C_{\text{HClO}} + K_3 \cdot C_{\text{ClO}_2}.$$

The view is therefore put forward that the kinetics of ClO_2 decomposition under these conditions is determined by two reactions:



The values of K_3 calculated from experimental data for 25, 35, and 50°, respectively are 0.022 ± 0.001 , 0.055 ± 0.001 , and 0.087 ± 0.002 .

3. Rate constants for the reaction $\text{ClO}_2 + \frac{1}{2}\text{Cl} + \text{H}_2\text{O} = \text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+$ at 10, 25, 35, 50, and 60° have been calculated. Their values are $1.1 \cdot 10^{-4}$, $1.5 \cdot 10^{-4}$, $3.0 \cdot 10^{-4}$, $11.7 \cdot 10^{-4}$, $26.7 \cdot 10^{-4}$, respectively.

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STUDY OF SOLUBILITY IN THE SYSTEMS $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$
AND $\text{Cr}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{H}_2\text{O}$

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Chromic oxide can be made from chromic chloride or nitrate, which are in their turn made from sodium chromate by reduction with sawdust (or other cellulosic material) in hydrochloric or nitric acid. For example, reduction of sodium chromate in hydrochloric acid gives chromic chloride and sodium chloride, and in nitric acid chromic nitrate and sodium nitrate are formed. If these salts could be separated and chromic chloride or nitrate were isolated in the pure state, they could be decomposed by heat to give chromic oxide.

Before carrying out technical trials of the production of chromic oxide from the chloride or nitrate, we studied the solubility relationships of sodium and chromic chlorides, and of sodium and chromic nitrates, in water at 20 and 80°.

The literature contains no information on solubility in the systems $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{H}_2\text{O}$.

The investigation was conducted by the isothermal method in a thermostat equipped with a rotating shaft. The solutions were contained in glass vessels with ground-glass stoppers, covered with rubber caps. The vessels were fixed in special nests on the shaft, and were rotated continuously by means of a motor.

The water temperature in the thermostat was regulated by a mercury-toluene thermoregulator. The temperature fluctuations in the thermostat were $\pm 0.1^\circ$.

When the composition of the liquid phase became constant, it was assumed that equilibrium had been reached. In some instances solution equilibrium was approached from both directions. The same results were obtained in each case. Samples were withdrawn by means of weighing pipets (with stopcocks and caps) which also served for density determinations. The tip of the pipet immersed in the solution was protected with a dense cotton-wool plug to prevent entry of crystals.

The composition of the solid phase was determined graphically by the method of "residues." Sodium chloride and sodium nitrate were easily visible with the naked eye. Crystals of chromic nitrate nonahydrate were deep violet in color. Crystals of chromic chloride hexahydrate were green.

Tie lines lead accurately to the points for the composition of the corresponding salts. Samples of the solid phase were collected after filtration on a No. 2 Schott filter. Previously-heated filters were used for filtration of the solutions at 80°.

Diluted solutions of the liquid samples and solid phases were kept in flasks. Diluted solutions of the nitrate system had a blue-violet color right from the start. Solutions of the chloride system were initially bright green. On standing, the dilute solutions gradually turned blue-green and then blue-violet.

Analytical methods. Trivalent chromium was determined volumetrically after oxidation to sexivalent chromium by hydrogen peroxide in alkaline solution. A sample of the oxidized solution with added sulfuric acid was titrated by 0.1 N solution of Mohr's salt in presence of phenylanthranilic acid as indicator [1].

Sodium was determined in chromic chloride solutions by determination of chloride. Chromic nitrate was converted into chloride by treatment with hydrochloric acid, and the sodium content was determined as stated above.

Chloride was determined by titration of aliquot portions with mercuric nitrate in aqueous alcohol. The indicator was 0.1% alcoholic solution of diphenylcarbazide. The volumetric method for determination of chloride by titration with silver nitrate solution (the Volhard method) in an acid medium is not suitable because of the color of chromic solutions.

EXPERIMENTAL

Isothermal data for the ternary system $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$ at 20 and 80° are given in Table 1 and in Figs. 1 and 2. The solutions were agitated for 2 to 4 days at these temperatures.

TABLE 1
Solubility in the System $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$

Points	Density	Solution				Residue (wt.%)		Solid phases
		CrCl_3 wt. %	NaCl	CrCl_3 g per 100 g H_2O	NaCl	CrCl_3	NaCl	
20° isotherm								
A	1.450	40.70	—	68.63	—	53.12	—	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
B	1.456	39.96	0.36	66.96	0.60	43.53	18.79	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O} +$ + NaCl
2	1.421	37.14	0.88	59.93	1.42	4.35	90.23	
3	1.400	35.37	1.33	55.88	2.10	4.96	86.65	
4	1.284	20.45	9.77	29.31	1.40	1.96	92.34	
5	1.241	11.22	16.88	15.61	23.48	Traces	95.77	
6	1.214	4.08	23.07	5.61	31.67	Traces	99.05	
C	—	0	26.38	—	35.83	—	—	
80° isotherm								
A	—	54.28	—	118.73	—	58.04	—	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
B	1.632	53.80	2.13	122.07	4.83	51.04	11.96	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O} +$ + NaCl
1	1.608	52.34	2.32	115.44	5.12	13.05	76.20	
2	1.609	48.96	3.07	102.07	6.40	8.07	85.83	
3	1.572	47.57	4.09	98.41	8.47	12.81	75.28	
4	1.312	37.44	5.69	65.84	10.00	4.60	89.06	
5	1.369	31.07	7.25	50.37	11.76	0.90	97.26	
6	1.225	10.41	19.55	14.67	27.92	0.70	98.91	
C	—	0	27.54	—	37.72	—	—	

No supersaturation effects were observed in these solutions. The 20° isotherm was studied in the range of 4.08 to 40.70% CrCl_3 and 0.36 to 26.38% NaCl.

The 80° isotherm was studied in the range of 10.41 to 54.28% CrCl_3 and 2.13 to 27.54% NaCl.

On the 20 and 80° isotherms the point A corresponds to the composition of saturated chromic chloride solution. The point C corresponds to the composition of aqueous saturated sodium chloride, the solubility of which varies very little with temperature [2].

The solubility of chromic chloride at these temperatures falls sharply with increase of sodium chloride concentration. The point B corresponds to the composition of a solution saturated with chromic chloride and sodium chloride (the eutonic point). Points along the line AB correspond to compositions of saturated solutions in equilibrium with chromic chloride. Points along the line BC correspond to compositions of saturated solutions in equilibrium with sodium chloride.

The 20 and 80° isotherms do not show any breaks which might indicate the formation of a double salt.

As the solutions are evaporated at 80° down to 50-52% CrCl_3 in solution, sodium chloride separates out while chromic chloride remains in solution. After separation of sodium chloride, the chromic chloride must be dehydrated, and chromic oxide can then be obtained by calcination.

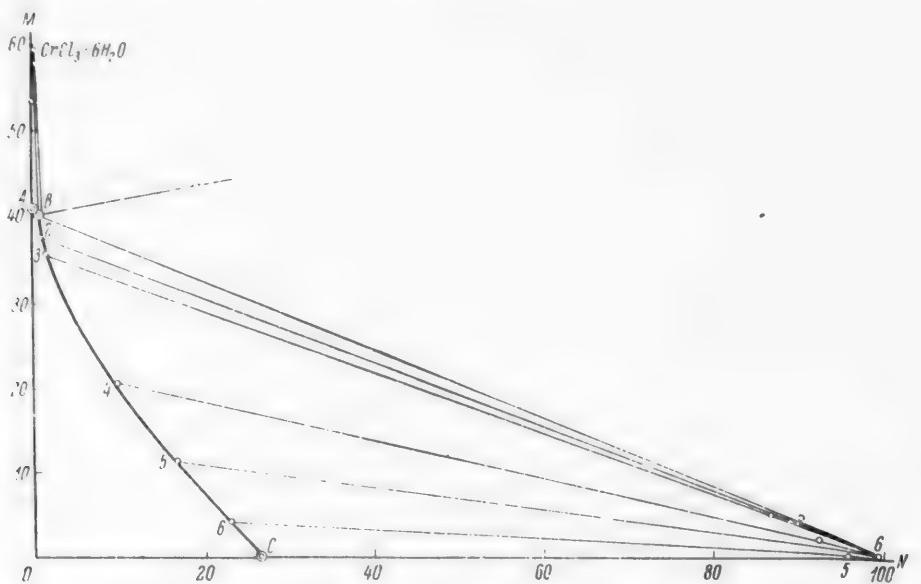


Fig. 1. Solubility in the system $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$ at 20°: M) CrCl_3 content (in weight percent); N) NaCl content (in weight percent).

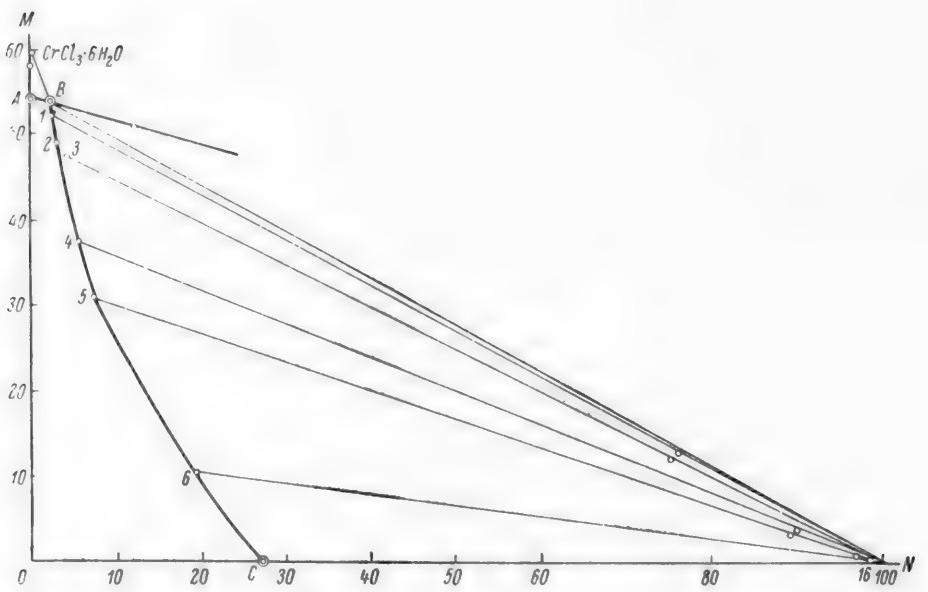


Fig. 2. Solubility in the system $\text{CrCl}_3 - \text{NaCl} - \text{H}_2\text{O}$ at 80°. M) CrCl_3 content (in weight percent); N) NaCl content (in weight percent).

The results of isothermal studies of the system $\text{Cr}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{H}_2\text{O}$ at 20 and 80° are given in Table 2 and Figs. 3 and 4.

The 20° isotherm was studied in the concentration range of 14.26 to 42.07% $\text{Cr}(\text{NO}_3)_3$, and 0.69 to 46.18% NaNO_3 . It is seen in Fig. 3 that the point A represents the solubility of chromic nitrate in water. The point C represents the solubility of sodium nitrate in water; this increases considerably with temperature [3].

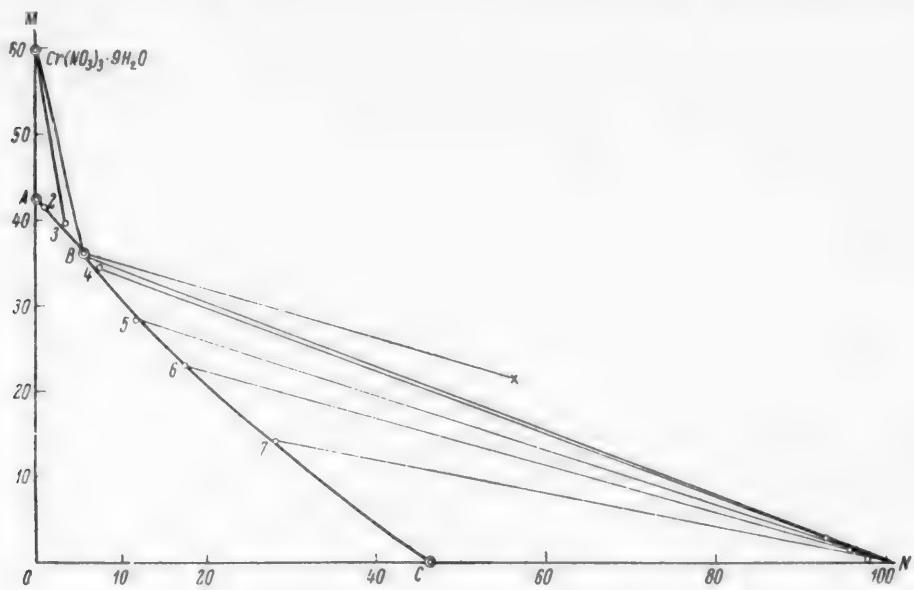


Fig. 3. Solubility in the system $\text{Cr}(\text{NO}_3)_3-\text{NaNO}_3-\text{H}_2\text{O}$ at 20°: M) $\text{Cr}(\text{NO}_3)_3$ content (in weight percent); N) NaNO_3 content (in weight percent).

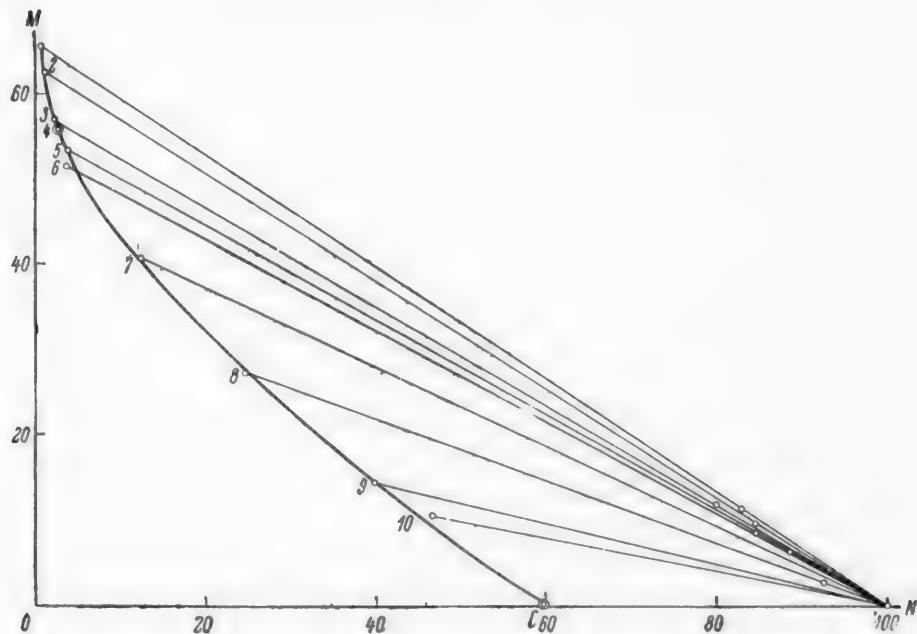


Fig. 4. Solubility in the system $\text{Cr}(\text{NO}_3)_3-\text{NaNO}_3-\text{H}_2\text{O}$ at 80°: M) $\text{Cr}(\text{NO}_3)_3$ content (in weight percent); N) NaNO_3 content (in weight percent).

The solution containing 35.87% $\text{Cr}(\text{NO}_3)_3$ and 5.08% NaNO_3 is eutonic, and is denoted by the point B in the diagram.

It follows from Fig. 3 that the 20° isotherm in the region studied consists of a short saturation branch in equilibrium with solid $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in the concentration range from 42.07 to 35.87% $\text{Cr}(\text{NO}_3)_3$. The long saturation branch in equilibrium with solid NaNO_3 extends from 0 to 35.87% $\text{Cr}(\text{NO}_3)_3$.

The 80° isotherm was studied in the concentration range of 0 to 65.35% $\text{Cr}(\text{NO}_3)_3$ and 0.67 to 59.70% NaNO_3 . Figure 4 shows that the isotherm consists of one long saturation branch in equilibrium with solid NaNO_3 .

TABLE 2
Solubility in the System $\text{Cr}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{H}_2\text{O}$

Points	Density	Solution				Residue (wt. %)		Solid phases
		$\text{Cr}(\text{NO}_3)_3$	NaNO_3	$\text{Cr}(\text{NO}_3)_3$	NaNO_3	$\text{Cr}(\text{NO}_3)_3$	NaNO_3	
		wt. %	g per 100 g H_2O					
20° isotherm								
1	1.460	42.07	—	72.62	—	56.80	—	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
2	—	41.28	0.69	71.14	1.19	57.62	—	
3	1.504	39.60	3.50	69.59	6.15	55.23	1.89	
B	1.520	35.87	5.08	60.75	8.60	21.63	56.24	
4	1.472	34.68	7.69	60.18	13.35	2.88	93.16	
5	1.434	28.54	11.87	47.89	19.92	1.88	95.38	
6	1.408	22.84	17.54	38.31	29.42	—	—	NaNO_3
7	1.372	14.26	28.13	24.75	49.83	0.44	97.83	
C	—	0	46.18	—	85.80	—	—	
80° isotherm								
1	1.756	65.35	0.67	192.32	1.97	11.40	82.90	NaNO_3
2	1.768	62.27	1.25	170.70	3.43	11.94	79.97	
3	1.719	56.80	2.01	137.90	4.88	10.56	84.65	
4	1.763	55.99	2.73	135.64	6.61	—	—	
5	1.692	53.04	3.98	123.41	9.26	9.86	84.87	
6	1.672	51.50	3.66	114.85	8.16	6.41	88.60	
7	1.575	40.82	12.55	87.54	26.92	2.41	92.53	
8	1.521	27.15	24.55	57.40	51.90	2.22	92.94	
9	1.482	14.71	39.80	32.34	87.49	—	—	
10	1.488	10.85	46.47	25.42	108.88	Traces	96.77	
C	—	0	59.70	—	148.14	—	—	

These isotherms show a sharp decrease in the solubility of chromic nitrate in the solutions. The field of chromic nitrate nonahydrate decreases with rise of temperature, and vanishes completely at 80°. The reason is that chromic nitrate nonahydrate melts below 80°, while other hydrates of chromic nitrate are not formed in presence of sodium nitrate which does not have dehydrating properties, like aqueous solutions of nitric acid [4].

The results of this investigation show that it is not possible to isolate sodium nitrate completely from solution by evaporation at 80° if the evaporation is continued until the chromium content in solution corresponds to the composition of chromic nitrate nonahydrate, i.e., to 59.38% $\text{Cr}(\text{NO}_3)_3$. There would always be about 2% NaNO_3 in such a solution; during subsequent drying and calcination this sodium nitrate would react with chromium oxide to form sodium chromate and dichromate, with a decrease in the yield of chromium oxide.

The sodium nitrate content of the evaporated solution can be reduced if the chromic nitrate content is raised to 64-65%, and the evaporation is continued until partial dehydration of melted nonahydrate begins. After some of the water from the nine molecules is lost, chromic nitrate does not crystallize out for a long time even after the temperature has been lowered somewhat, and sodium nitrate can be isolated completely from such a solution. Technical trials are necessary in order to determine whether evaporation to such high $\text{Cr}(\text{NO}_3)_3$ concentrations is feasible.

SUMMARY

1. Solubility diagrams of the ternary systems $\text{CrCl}_3-\text{NaCl}-\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3-\text{NaNO}_3-\text{H}_2\text{O}$ can be used for finding conditions for separation of chromic and sodium chlorides and of chromic and sodium nitrates.

After separation of the corresponding sodium salts, saturated solutions of chromic chloride and nitrate contain 1-1.5% of sodium chloride and 2% of sodium nitrate, respectively.

2. These results can be used as a basis for technical trials and for a possible process for the production of chromic oxide from chromate liquors by reduction with cellulose in hydrochloric or nitric acid solutions.

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DETERMINATION OF THE EXCHANGE CAPACITY OF SULFONATED CATION-EXCHANGE RESINS IN DYNAMIC CONDITIONS

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At the present time differences of opinion still exist on the question of standard methods for determination of exchange capacity of ion exchangers, and in particular, methods for determination of total exchange capacity.

This is largely due to the fact that there is as yet no agreement concerning the nature of this most important characteristic of ion exchangers. The most suitable concept of total exchange capacity is the value corresponding to the contents of active groups of a definite type, such as sulfo groups, carboxyl groups, etc., in the resin.

Table 1 contains the results of comparative experiments on determination of total exchange capacity of sulfonated cation exchangers. The determinations were performed by the dynamic method by passage of sodium chloride solution through a layer of resin, the under static conditions by titration of a sample of the resin in presence of excess sodium chloride solution, with methyl orange as indicator [1, 2].

TABLE 1
Results of Comparative Determinations of Total Exchange Capacity of Sulfonated Cation Exchangers

Resin	Active groups	Exchange capacity (meq/g) and determination conditions	
		dynamic	static
KU-2	SO ₃ H	4.92	4.94
KU-1	SO ₃ H; OH (phenolic)	2.23	2.25
SN	The same	2.30	2.33
SN	The same	3.17	3.21

Both methods are equally suitable for determinations of sulfo groups in ion exchangers, and give virtually identical results.

The resin-titration method is to be preferred. It is simpler and requires less time and reagents.

The authors of standard methods for determination of total exchange capacity of ion exchangers in dynamic conditions (E_d) do not always take into account differences in the rates of ion-exchange reactions with different ion exchangers, and therefore do not allow for possible low results.

For example, in the methods of Kunin and Myers and of Fisher and Kunin, a sample of sulfonated cation exchanger in the H form (5 g) is treated in a funnel with 0.27 N (1.5%) CaCl₂ solution [3], or with 0.56 N (4%) Na₂SO₄ solution [5], the filtrate is collected in a 1 liter measuring flask, and aliquot portions are titrated. The filtration rate is not given in the description of the method.

Since there is no check that the exchange reactions are complete, there is no certainty that 1 liter of solution is enough for complete replacement of H ions in the SO_3H groups by metal ions in all resins, and that low values of E_d are not obtained [5]. This is illustrated by the data in Table 2.

TABLE 2
Effect of Filtration Rate on the Amount of 0.5 N NaCl
Required to Replace H Ions in the Sulfo Groups of KU-1
Resin by Sodium Ions

Filtration rate of NaCl solution through a funnel with 5 g* of KU-1 resin (m/hour)	Amount of NaCl solution required for complete exchange reaction (ml)
2.5	1650
5	1800
10	1950

* Calculated for air-dry resin; moisture content 18%.

An important technical characteristic of ion exchangers is the exchange capacity to "breakthrough" of the extracted ions into the filtrate; this is known as the breakthrough capacity (E_b).

Methods for determination of E_b have been worked out in greatest detail in relation to the specific characteristics of water softening and deionization.

The GOST specifications for ion-exchanger tests [6, 7] proposed by the Ministry of Electrical Power Stations USSR, are very detailed, but are of a specialized character.

The values of E_b of ion exchangers depend on numerous factors (nature of the solute in the treated solution, solution concentration and filtration rate, height of the resin layer and grain size, nature of the regenerating substance, its concentration, total quantity, filtration rates, etc.).

Even if the conditions of E_b determinations are reproduced exactly, the results can show quite considerable variations, caused by factors which cannot be taken into account.

For example, the configuration and volume of "dead spaces" which may occur between the resin grains cannot be predicted.

If methods of different sensitivity are used for determination of breakthrough, different values of E_b are obtained for the same resin.

In this paper we consider very briefly, in the light of published and our own data, the influence of the height of the filtering layer, filtration rate, and grain size on the breakthrough exchange capacity.*

Unfortunately, at the present time there are no generally accepted methods of determination of E_b by any particular scheme of cation or anion exchange, and the influence of the above-mentioned factors on E_b is not always taken sufficiently into account.

All the conditions under which E_b is determined must be considered and indicated; otherwise the values obtained for E_b must be regarded as approximate at best. There is still less sense in citing values for E_b of ion exchangers without any indication of the determination conditions [8].

Conditions for determination of E_b of strongly acid ion exchangers in the hydrogen cycle, used by certain Russian workers or specified by GOST, are given in Table 3.

* V. S. Matrosova and T. V. Gerasimyuk took part in the experimental work.

TABLE 3

Conditions for Determinations of the Breakthrough Exchange Capacities of Strongly Acid Ion Exchangers in the Hydrogen Cycle *

Dimensions of water-swollen resin layer**			Filtration rate (cm/hour)	Grain size of air-dry resin (mm)	Solution used to determine ex-change capacity		Method for detection of breakthrough of the extracted ion in filtrate	Literature
dia-meter (cm)	height (cm)	volume (ml)			dissolved com-pound	solution conc. meq liter		
1.65	(47)	100	10	0.25—1.7	CaCl ₂	3.5	1) By decrease of acid concentration in filtrate; titration with 0.1 N NaOH in presence of Methyl orange; 2) by calcium content; titration with alcoholic solution of potassium oleate; residual Ca ⁺⁺ concentration not higher than 0.5 meq/liter.	[6,7]
2.5	(20.4)	100	1.5	0.3—2.0	CaCl ₂	7.0	By decrease of acid concentration in filtrate; titration with 0.02 N NaOH in presence of Methyl orange	[9]
2.5	40 25	(196)*** (123)	7.5	0.2—2.0	CaCl ₂	7.0	Analytical method not stated. Determination ends at filtrate hardness of 0.05 meq/liter	[10]
1.8	55—60 (140—153)	—	—	0.6—0.75	CaCl ₂	3.5	Method for determination of breakthrough not stated	[11]
(1.46)	50	83	10	0.6—0.75	Chlorides Na, K, NH ₄ , Cs, Ag, Be, Mg, Ca, Cu, Sr, Cd, Ba, Pb, Mn, Ni, Co	3.5—3.7	By decrease of acid concentration in filtrate; determination ends when difference of H ion concentrations in the filtrate and original solution reaches 0.04 to 0.05 meq/liter	[12]

* Results recalculated in the same units.

** Figures in parentheses calculated from other dimensions given.

*** Two different heights of the swollen-resin layer are given [10] on pp. 101-102 and 115.

It is sometimes recommended to determine E_b with the use of relatively large amounts of resins, but in layers of only moderate height [9, 10]. However, E_b depends much more on the layer height than on the total volume occupied by the material. Myers, Eastes, and Myers [13] used columns from 1.25 to 10 cm in diameter for determination of E_b and always obtained identical results in determinations with columns of large and small diameters.

The influence of the height of sulfonated cation exchanger layers on E_b is illustrated in Table 4.

TABLE 4
Effect of Layer Height on the Breakthrough Exchange Capacity of Sulfonated Cation Exchangers*

Sulfonated resins	Dimensions of water-swollen resin layer		E_b (meq/liter)
	height (cm)	volume (ml)	
Wofatit KS	17.6	20	785
	44.0	50	950
SN	17.6	20	535
	44.0	50	630

* Working solution, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 14 meq/liter; filtration rate 5 m/hour; resin grain size 0.5-1.0 mm; column diameter 12 mm; regenerating solution, 2N HCl.

Meleshko's investigations [14] confirmed that the views of Shilov and his associates [15] on the dynamics of gas and vapor sorption are applicable to ion exchange.

According to his results, the amount of alkali solution required for titration of the filtrate collected during the passage of neutral salt solution through the resin column, from the instant of breakthrough to final saturation of the resin, does not change with the height of the resin layer if all the other conditions remain constant. The exchange capacity corresponding to this amount of alkali solution, the "final saturation capacity" (E_s), increases with increase of column diameter at constant resin weight, and E_b therefore decreases. The increase of E_s is proportional to the increase of column radius.

It was thus shown that the dimensions of filters of large heights or diameters can be calculated from the results of laboratory tests with small filters.

The filtration rates of the solutions through resin layers, recommended by different authors, differ considerably. E_b depends to a great extent on the filtration rate. However, systematic studies of this dependence are not specified in any of the consecutive versions of GOST 5695 for tests of ion exchangers [6, 7, 16].

Neither is sufficient attention paid to the influence of grain size on E_b . This influence is considerable. Table 5 contains values calculated from Prokhorov's data [17] for a sulfonated cation exchanger.

TABLE 5
Effect of Grain Size on the Breakthrough Exchange Capacity of Sulfonated Cation Exchangers
(Prokhorov's data)

Grain size (mm)	E_b relative to 1.5-2 mm fraction
1.5-2.0	1.00
1.0-1.5	1.28
0.5-1.0	1.91
0.2-0.5	3.05

The grain sizes (1-1.5 mm) of the resin fractions recommended by GOST 5695-52 [16] for determinations of E_d and E_b are too large. Prokhorov and Yankovskii [12] and Prokhorov and Korneeva [11] drew attention to the need to use narrow resin fractions for more accurate determination of E_b .

Table 6 shows the influence of layer height, filtration rate, and grain size on the exchange capacities of KU-1 and SBS-R sulfonated cation exchangers.

TABLE 6
Effect of the Height of Filtering Layer, Filtration Rate, and Grain Size on the Breakthrough Exchange Capacity of Sulfonated Cation Exchangers*

Resin grain size (mm)	E_b (meq/liter) with filtering layer height (mm)			
	20.5		10.25	
	filtration rate			
	5	2.5	2.5	1.25
KU-1 sulfonated phenolic resin				
0.5-1.0	605	666	—	—
1.0-1.5	420	522	400	525
SBS-R sulfonated coal resin				
0.5-1.0	609	705	587	628
1.0-1.5	431	511	371	452

* Working solution, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 14 meq/liter; regenerating solution, 2 N HCl.

The data in Table 6 must be regarded as tentative. Few experiments were performed, and the fractions of grain sizes were too wide.

The values of E_b for 0.5-1.0 mm fractions were 1.3-1.6 times the values for 1.0-1.5 mm fractions.

It is evident that E_b for different batches of the same resin, containing grains in the generally recommended ranges of 0.25-1.5 or 0.25-2.0 mm, may fluctuate considerably according to the predominance of larger or smaller grains in such wide fractions. At the same filtration rate ($v = 2.5$ m/hour), E_b for a resin layer 20.5 cm high is 1.2-1.4 times the value of E_b for a layer half that height. With 20.5 cm layers E_b at $v = 5$ m/hour is 1.1-1.2 times E_b at $v = 2.5$ m/hour; with a 10.25 cm layer E_b at $v = 2.5$ m/hour is 1.2-1.3 times the value at $v = 1.25$ m/hour.

The selection of rapid and adequately sensitive methods for determination of breakthrough of ions into the filtrate is important.

Methods for determination of residual hardness of solutions by determination of the end of foaming in titration of filtrate samples with fatty-acid salts [18] are still of importance at the present time [6, 7].

In cation treatment in the hydrogen cycle, breakthrough is usually indicated by the start of a decrease in the acid concentration in the filtrate, but the permissible decrease of filtrate acidity is generally not indicated.

If small amounts of resin are used for determination of E_b , the filtrate is collected in small portions (25 to 50 ml) and 0.1-0.025 N alkali is used for titration, it becomes rather difficult to detect the decrease in the amount of alkali solution due to presence of traces of the extracted cation in the filtrate.*

In the case of sulfonated cation exchangers, which are still mainly used for water softening, a very important test is determination of breakthrough exchange capacity with the aid of calcium salts (usually CaCl_2).

* For example, if the permissible filtrate hardness is 0.035 meq/liter (0.1° H), detection of this hardness in titration of 50 ml of filtrate requires only 0.018 ml less of 0.1 N NaOH solution than would be needed for titration of a sample without breakthrough.

Copper sulfate solutions were used in our experiments. It was found that very similar E_b values for sulfonated cation exchangers are obtained with the use of calcium and copper salts. This observation agrees with the results of Prokhorov and Yankovskii [12].

The presence of copper ions in the filtrate can be detected by rapid and simple methods.

The use of copper salts for determinations of exchange capacity of cation exchangers is reported in a number of publications.

Fieger, Gray, and Reed [19] used copper nitrate solution, and Siling [20] used copper acetate solution for determination of the total exchange capacity of soils. The copper content of the solution separated from the soil was determined electrolytically, or colorimetrically as the cuprammonium complex. Gapok and Zhupakhina [21] used copper nitrate solution for determination of the dynamic exchange capacities of permutite, glauconite, and various soils; copper in the filtrate was determined iodometrically.

Several methods for detection of copper in the filtrate were used in our determinations of E_b of cation exchangers. Colorimetric determination of copper as the ammine can detect only down to 0.2 mg of copper in 50 ml of solution [22], which corresponds to 0.125 meq/liter ($0.35^{\circ}H$).

The method with potassium ferrocyanide proved to be the most suitable. Traces of copper in the filtrate were indicated by a reddish color in the solution. Further accumulation of copper in the filtrate caused the appearance of a red-brown precipitate.

In presence of strong acids, cupric ions give a distinct reaction with potassium ferrocyanide with $14 \cdot 10^{-6}$ g of copper per 10 ml of solution, which corresponds to $4.4 \cdot 10^{-2}$ meq/liter ($0.123^{\circ}H$).

Copper sulfate solutions were used in our experiments, and copper was therefore determined in presence of sulfuric acid. According to [23], the sensitivity of the method for determination of copper should increase to $9.3 \cdot 10^{-3}$ meq/liter ($0.026^{\circ}H$), or almost five-fold in acetic acid solution.

Our procedure for laboratory determination of the breakthrough exchange capacity of sulfonated cation exchangers was as follows.

Resin fractions of 0.5-1.0 or 0.25-0.5 mm were taken* in amounts to give swollen volumes of 25 or 50 ml. Each sample was transferred, together with water, to a dynamic-test tube of 12 mm inner diameter, with a sealed-in glass bottom with perforations of about 0.2 mm.

Air bubbles were expelled from the water-covered resin. The swollen resin layer was about 22 or 44 mm high with volumes of 25 or 50 ml respectively. Copper sulfate solution of concentration 14 meq/liter was put in a flask attached to the upper end of the tube. The filtration rate was regulated by means of a stopcock at the lower end of the tube, and was usually kept at 2.5 or 5 m/hour. Filtrate samples were collected in 25 ml measuring cylinders and tested for breakthrough of copper ions by addition of 2-3 crystals of potassium ferrocyanide. When traces of copper appeared in the filtrate the percolation was stopped, the resin was washed several times with water, and then regenerated (usually at a filtration rate of 2.5 m/hour) by 2 N hydrochloric acid. To check completeness of regeneration, the filtrate was titrated by 0.1 N NaOH solution in presence of Methyl orange, and finally tested for possible presence of copper ions by means of potassium ferrocyanide. The resin was then washed free of hydrochloric acid with distilled water to a neutral reaction.

We consider that the GOST specifications for tests on ion exchangers should give details of simple apparatus, suitable for routine laboratory tests, for determinations of the breakthrough exchange capacity of ion exchangers with small samples, about 10-20 g, under standard conditions. These methods would enable research workers synthesizing and studying ion exchangers to perform comparative tests on new resin samples with little expenditure of time and reagents. As was pointed out earlier, the possibility of design calculations relating to filters of large height and diameter based on results of E_b determinations in small filters [14] is worthy of special attention. Apparatus of the type described here need not prevent the use, especially in specialized laboratories, of larger and better equipment for detailed tests on selected best batches of resins.

* Narrower grain fractions should be taken for more accurate determinations.

SUMMARY

1. There are no consistent methods for determinations of the exchange capacity of sulfonated ion exchangers under dynamic conditions, and the numerous factors influencing this value are not adequately taken into consideration.

2. Simple laboratory equipment should be devised for standard comparative determinations of the breakthrough exchange capacity of small samples of ion exchangers, with small expenditure of time and reagents.

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF LIQUID METALLIC SOLUTIONS OF POTASSIUM AND BISMUTH

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Investigation of the thermodynamic properties of liquid metallic solutions is an important step in the development of a general theory of solutions. Systems characterized by strong interaction are of particular importance. Such systems include K-Bi alloys. According to the phase diagram [1], potassium and bismuth form three compounds: K_3Bi , melting congruently at 671° ; K_3Bi_2 , melting incongruently at 420° , and KBi_2 , melting incongruently at 553° . Therefore, liquid metallic K-Bi solutions should show extremely large negative deviations from the Raoult law.

The thermodynamic properties of potassium were calculated from the electromotive forces (emf) of the cells:

potassium | electrolyte with potassium ions | potassium (N_K) + bismuth (N_{Bi}), where N_K and N_{Bi} are atomic fractions of the solution components.

The electrolyte used was 3S-5 "K" solid glass, containing 5% K_2O . The possibility of using glass for such investigations has been demonstrated earlier [2, 3].

The activity of potassium was calculated from the emf by the equation

$$\lg a_K = -\frac{5040 \cdot E}{T}.$$

The state of pure liquid potassium at the same temperature was taken as the standard state. The partial values of the isobaric-isothermal potential ($\Delta\bar{Z}_K$) and excess potential ($\Delta\bar{Z}_K^*$) were calculated from the equations:

$$\begin{aligned}\Delta\bar{Z}_K &= -23060 \cdot E = 4.576 \cdot T \cdot \lg a_K, \\ \Delta\bar{Z}_K^* &= \Delta\bar{Z}_K - RT \ln N_K = 4.576 \lg \frac{a_K}{N_K} = 4.576 \cdot T \cdot \lg \gamma_K.\end{aligned}$$

The partial molar entropy of mixing ($\Delta\bar{S}_K$) is

$$\Delta\bar{S}_K = 23060 \frac{dE}{dt}.$$

The partial molar heat of mixing was calculated from the expression

$$\Delta\bar{H}_K = \Delta\bar{Z}_K + T \cdot \Delta\bar{S}_K.$$

Thermodynamic data for the second solution component were calculated by graphical integration from the Gibbs-Duhem equation

$$\lg \gamma_{\text{Bi}} = - \int_0^{N_K} \frac{N_K}{N_{\text{Bi}}} d \lg \gamma_K.$$

Integral values were calculated from the equation

$$\Delta G = (1 - N_K) \int_0^{N_K} \frac{\Delta \bar{G}_K}{(1 - N_K)^2} dN_K,$$

where ΔG_K is any partial thermodynamic function of state.

EXPERIMENTAL

The design of the measurement cell was as described previously [4, 5]. The experiments were conducted in an atmosphere of thoroughly purified argon. Bismuth of high purity was used in the work. To remove any sodium, metallic potassium was filtered in an atmosphere of nitrogen containing a small amount of oxygen [6]. The potassium was then passed through a narrow capillary into thin-walled glass ampoules, which were then sealed. Exact weights of potassium could be taken in this way. The emf was measured to an accuracy of $\pm 0.2 \text{ mV}$, with the aid of a PPTV 1 potentiometer and a mirror galvanometer sensitive to $1 \cdot 10^{-9} \text{ amp}$. The reproducibility of the results in either temperature direction was within $\pm 0.5 \text{ mV}$. The temperature was measured by means of a chromel-alumel thermocouple and a galvanometer with 5° scale divisions. The determinations were performed at 525–580°. Our method cannot be used for measurements at temperatures above 580–600°. The system K–Bi was therefore studied only in the bismuth-rich composition region; the investigation covered the concentration range N_K from 1.0 to 0.85 and from 0.70 to 0.05 at 575°. It has been reported [1] that the system is heterogeneous in the N_K range from 0.84 to 0.75 at 575°. The emf temperature coefficients dE/dT were determined fairly reliably for alloys poor in potassium ($N_K < 0.75$). The heterogeneity regions in all the diagrams (Figs. 1–3) are indicated by dash lines.

DISCUSSION OF RESULTS

The emf of the cell: potassium | glass | potassium–bismuth alloy at 575° for different alloy compositions, the temperature coefficients of emf, and the calculated activities and activity coefficients, are given in Table 1.

TABLE 1
Emf of the Cell Potassium | Glass | Potassium–Bismuth Alloy, Activity and Activity
Coefficient of Potassium, and Temperature Coefficient of emf for Different Alloy
Compositions at 575°

N_K	emf (v)	a_K	γ_K	dE/dT	N_K	emf (v)	a_K	γ_K	dE/dT
0.05	0.969	0.00000174	0.00003488	-0.00004	0.37	0.6525	0.0001325	0.0003581	-0.00042
0.08	0.934	0.000002815	0.00003518	-0.00008	0.42	0.606	0.0002504	0.0005961	-0.00036
0.11	0.911	0.000003856	0.000035	-0.00022	0.43	0.6025	0.0002627	0.00061093	-0.0004
0.13	0.888	0.000003856	0.0000296	-0.00018	0.53	0.446	0.002236	0.004218	-0.00044
0.15	0.886	0.000005428	0.0000361	-0.0003	0.55	0.459	0.001872	0.0034036	-0.00006
0.15	0.880	0.00000593	0.0000392	-0.00028	0.57	0.423	0.003063	0.005373	-0.00036
0.15	0.854	0.000008411	0.000056	-0.00004	0.58	0.394	0.005316	0.0091655	-0.00044
0.24	0.7-8	0.00002075	0.00008645	-0.00012	0.60	0.370	0.006327	0.010545	-0.000152
0.25	0.774	0.00002513	0.0001	-0.00016	0.60	0.366	0.006682	0.011136	-0.000184
0.25	0.762	0.00002962	0.000118	-0.00008	0.60	0.371	0.006241	0.010401	+0.000016
0.3	0.738	0.00004114	0.000137	-0.00002	0.9	0.016	0.8034	0.89266	-0.00006
0.33	0.695	0.00007409	0.000224	-0.004	0.9	0.025	0.7103	0.78922	
0.34	0.678	0.00009349	0.00027497	-0.00024	0.92	0.0172	0.7903	0.85902	-0.000006
0.35	0.684	0.00008613	0.000246	-0.00048	0.93	0.019	0.7711	0.82913	-0.00024
0.35	0.6895	0.00007988	0.000228	-0.0003	0.95	0.007	0.9087	0.95652	-0.00012
0.37	0.655	0.0001281	0.0003462	-0.0003					

Isotherms for activity (Curve 1) and activity coefficient (Curve 2) of potassium are plotted on a semi-logarithmic scale in Fig. 1. Liquid metallic K-Bi solutions exhibit extremely large negative deviations from ideal behavior. For example, for an alloy with $N_K = 0.5$ the activity is only 0.00018, and for an alloy with $N_K = 0.05$ it is 0.00000174. This behavior of liquid K-Bi solutions may be attributed to binding of potassium in stable structural groups of metallic compounds.

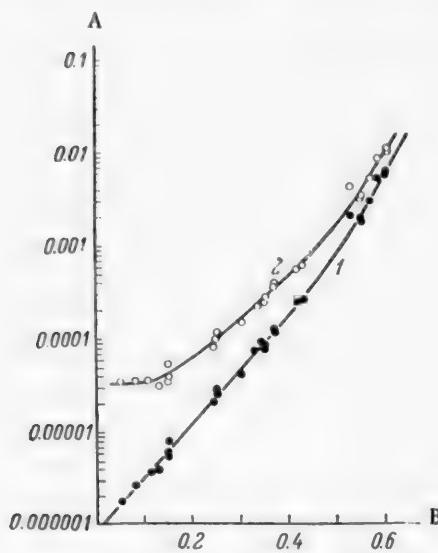


Fig. 1. Activity and activity coefficient of potassium at 575°: A) activity and activity coefficient of potassium; B) atomic fraction of potassium; curves: 1) activity, 2) activity coefficient.

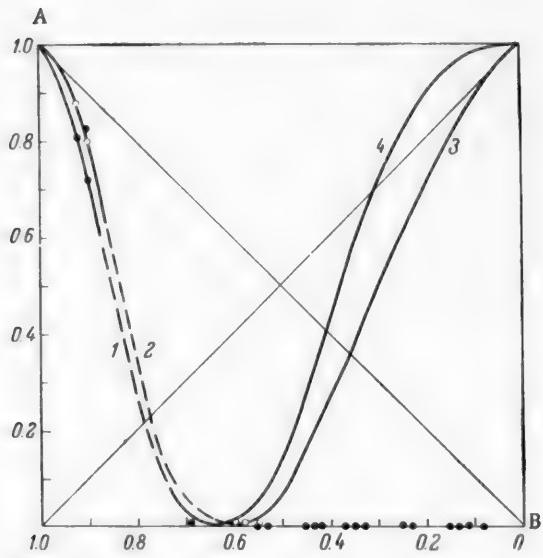


Fig. 2. Activity and activity coefficients of the components in K-Bi solution at 575°: A) activity and activity coefficient; B) atomic fraction of potassium; curves: 1) activity of potassium, 2) activity coefficient of potassium, 3) activity of bismuth, 4) activity coefficient of bismuth.

Partial and integral thermodynamic data for the system K-Bi at 575° are given in Tables 2 and 3, and Figs. 2 and 3. These data correspond to exact atomic fractions of potassium, and were found by graphical interpolation from smooth curves plotted from experimental data.

Figure 2 shows that the activity isotherm for bismuth (Curve 3) lies entirely in the region of negative deviations. Accordingly, the activity coefficient of bismuth is less than unity over the entire composition region. It should be noted that the relative positions of the activity isotherms for potassium and bismuth (Curves 1 and 3, respectively) are

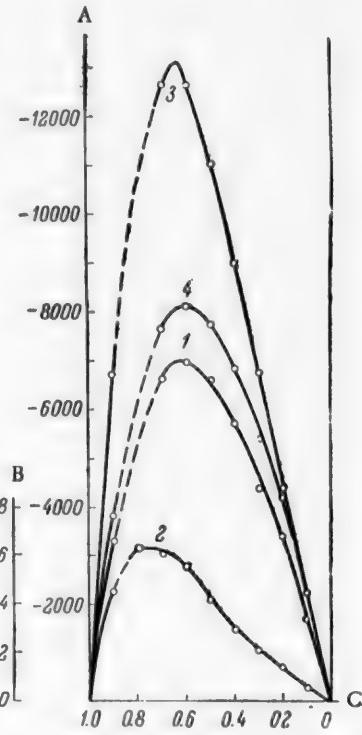


Fig. 3. Integral thermodynamic data for the system K-Bi at 575°: A) integral thermodynamic values of ΔZ , ΔZ^* , ΔH (cal/g-atom); B) integral excess entropy of mixing (cal/degree·g-atom); C) atomic fraction of potassium; 1) ΔZ^* , 2) ΔS^* , 3) ΔH , 4) ΔZ .

consistent with the general considerations put forward by Alabyshev and Lantratov [7] concerning the relationship between the form of the activity isotherm and the composition of compounds formed in the system.

TABLE 2
Integral Thermodynamic Data for the System at 575°

Data	Atomic fraction of potassium, N_K								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
ΔZ	-2260	-4260	-5410	-6870	-7770	-8120	-7690	-6310	-3840
ΔZ^*	-1714	-3420	-4380	-5740	-6600	-6990	-6660	-5470	-3295
ΔH	-2250	-4448	-6797	-9042	-11030	-12369	-12369	-10685	-6747
ΔS^*	-0.671	-1.48	-2.126	-2.978	-4.231	-5.635	-6.086	-6.258	-4.5612

The integral values of excess potential (Curve 1), excess entropy of mixing (Curve 2), heat of mixing (Curve 3), and potential (Curve 4) are plotted in Fig. 3. Each curve has a well-defined maximum. The presence of three compounds in the system resulted in some displacement of the maximum from the composition of the most stable compound K_3Bi . An important fact is that ΔS and ΔS^* ($\Delta S - \Delta S_{\text{ideal}}$) are negative over the entire concentration region. This is associated with the nature of the bonds in the metallic compounds formed in the system. According to Vetter and Kubaschewski [8], negative entropies in the middle concentration region are observed in the systems Mg-Bi (700-800°) and Mg-Sb (860-920°). The strong polarity of the bonds in these compounds was demonstrated experimentally by Kubaschewski and Reinartz [9]. Since metallic properties are more pronounced in potassium than in Mg, bond polarity should be stronger in potassium-bismuth compounds. The maximum value of ΔS^* in our case reaches 6.3 cal/degree·g-atom.

TABLE 3
Activity and Activity Coefficients of Bismuth at 600 and 550°

Temp. (in °C)	Activity and activity coefficient	Atomic fraction of potassium, N_K					
		0.1	0.2	0.3	0.4	0.5	0.6
600	α_{Bi}	0.8829	0.70888	0.49588	0.25812	0.071	0.005244
	γ_{Bi}	0.981	0.8861	0.7084	0.4302	0.142	0.01311
550	α_{Bi}	0.87498	0.6928	0.45283	0.20856	0.04525	0.001596
	γ_{Bi}	0.9722	0.866	0.6469	0.3476	0.0905	0.00399

SUMMARY

The emf method was used to determine thermodynamic data for liquid metallic solutions of K-Bi at 575°. The system showed extremely large deviations from ideal behavior. These deviations are due to strong interaction of the components.

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INFLUENCE OF SULFATE IONS ON THE ELECTRODEPOSITION OF CHROMIUM

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It is known that in electrolysis of chromic anhydride solutions either chromium is not deposited at all, or a black spongy deposit containing inclusions of chromium hydroxide and basic salts is formed on the cathode.

A satisfactory metal deposit can be obtained only in the presence of certain extraneous anions. The most effective anion, which is widely used in practice for electrodeposition of chromium, is sulfate.

There have been a number of investigations of the electrodeposition of chromium from chromate solutions [1-5], but the role of SO_4^{2-} ions is not yet fully understood. For example, Müller attributes their favorable effect to their ability to break down, at definite potentials, the chromic chromate film which covers the cathode during electrolysis.

Sulfate ions therefore assist penetration of the discharging ions to the cathode [2]. However, certain objections may be raised on close scrutiny of Müller's theory. It is difficult to understand how negative SO_4^{2-} ions can penetrate to the cathode through the film. It is likewise not clear why only these ions loosen the film, and only in the region of negative potentials; why other anions, such as $\text{Cr}_2\text{O}_7^{2-}$, Cl^- , NO_3^- , ClO_4^- , etc., do not have a favorable effect.

Because of these and certain other objections, other theories have been advanced on the mechanism of the action of sulfate ions. For example, Fink [3] suggested that SO_4^{2-} ions catalyze the cathode process.

Haring [5] assumed that the action of SO_4^{2-} ions is attributable to interaction with trivalent chromium in the colloidal state, by the following reaction:



However, Kasper [5] showed that $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ is a strong electrolyte, and that this salt is present in the electrolyte in true solution, and not in the colloidal state. Therefore, the above exchange reaction cannot take place. Kasper considered that complex ions of the type $[\text{Cr}_4\text{O}(\text{SO}_4)_4(\text{H}_2\text{O})_4]^{2+}$ are formed in the electrolyte and may be discharged at the cathode. The liberated sulfate ions then migrate to the anode. Moreover, SO_4^{2-} ions may be adsorbed by positively charged colloidal particles and thus retard their movement toward the cathode. It is easily seen that the $[\text{Cr}_4\text{O}(\text{SO}_4)_4(\text{H}_2\text{O})_4]^{2+}$ ion contains the Cr^{3+} cation which, in Kasper's opinion, is discharged at the cathode to give the metal.

However, recent work [6, 7] has shown that metallic chromium is formed from anions containing sexivalent chromium, and not from trivalent cations.

Our detailed studies of electrode processes in the electrodeposition of chromium [8-10] lead to certain conclusions concerning the role of SO_4^{2-} anions in the process. As has been noted repeatedly, a peculiarity of chromium electrolytes is that the metal is contained in the complex anions $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} which are in dynamic equilibrium:



At the CrO_3 concentrations used for electrodeposition of chromium the equilibrium is shifted completely in the direction of $\text{Cr}_2\text{O}_7^{2-}$ ion formation, i.e., in absence of current or at low current densities the electrolyte virtually consists of dichromic acid ($\text{H}_2\text{Cr}_2\text{O}_7$).

Nevertheless, in absence of extraneous ions such as SO_4^{2-} the reduction of chromate anions at the cathode proceeds with considerable retardation, as it is effected by direct reduction of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} anions:



At relatively low current densities (in the region of electrode potentials on the positive side of the discharge potential of hydrogen ions) Reaction (a) takes place; with further increase of current density, simultaneous discharge of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} anions begins at the cathode, together with liberation of hydrogen ions. (The explanation for this last fact is that the potential φ_{H_2} is reached with increase of D_{C} .)

Thus, $\text{Cr}_2\text{O}_7^{2-}$ ions are discharged with formation of Cr^{3+} in a definite potential region (before the potential of hydrogen evolution is reached).

When the hydrogen evolution potential is reached, hydroxyl ions appear at the cathode and their concentration increases rapidly. As the hydroxyl ions accumulate in the catholyte, they react with the Cr^{3+} ions formed in the discharge of $\text{Cr}_2\text{O}_7^{2-}$ ions, and this ultimately leads to formation of chromium hydroxide and basic salts which are deposited on the cathode in the form of a dense black film.

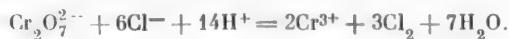
Our investigations showed that the cathode film in the fresh state is soluble in hot hydrochloric acid, giving a solution of a green color, characteristic of Cr^{3+} ions. The film is also soluble in hot alkali to give $[\text{Cr}(\text{OH})_6]^{3-}$ ions.

This led to the conclusion that the difficulties found in the electrodeposition of chromium in absence of sulfate ions are due to the formation of a protective film of chromium hydroxide, and basic salts, which prevents access and cathodic reduction of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions.

In that case the only possible cathode process is discharge of hydrogen ions. It may be assumed that in that case the pH of the catholyte layer very rapidly reaches the point of $\text{Cr}(\text{OH})_3$ formation, which is about 5.

Addition of sulfate ions to the electrolyte prevents formation of the passive cathodic film; this is because trivalent chromium is an effective complex former [11] and usually forms very stable complex compounds with SO_4^{2-} ions.

The explanation for the low effectiveness of other anions, such as Cl^- , I^- , etc., as compared with sulfate, is that in chromate electrolytes they are readily reduced by $\text{Cr}_2\text{O}_7^{2-}$ ions:



NO_3^- ions are also reduced at the cathode [12]; their reduction products have a particularly unfavorable effect on the quality of the chromium coatings, causing the appearance of dark bands, sponginess, etc. The ions PO_4^{3-} , ClO_4^- do not form stable complex ions with Cr^{3+} .

Cr^{3+} ions form complex compounds of different composition with sulfate anions; the composition depends to a great extent on the solution temperature [13]. At low (room) temperatures the violet modification is formed, in which Cr^{3+} and SO_4^{2-} display their most characteristic individual properties. When heated, the violet modification gradually passes into the green; here Cr^{3+} and SO_4^{2-} are contained in the inner sphere of a stable complex ion, and as a result the ions constituting the complex no longer display their characteristic properties and reactions. Thus, we may conclude that the favorable effect of SO_4^{2-} ions on the electrodeposition of chromium is due to the formation of unreactive stable complex ions of trivalent chromium with sulfate ions. This prevents the formation of films consisting of sparingly soluble basic salts and chromium hydroxide, which make the cathode surface passive. This conclusion is consistent with the experimental fact that increase of temperature has a favorable effect on chromium plating, because interaction between Cr^{3+} and SO_4^{2-} ions is facilitated at higher temperatures (the degree of hydration decreases and ionic mobility increases). Apart from the fact that sulfate ions form stable complexes with trivalent chromium ions, they are also adsorbed by colloidal particles.

The adsorption of different anions by colloidal particles decreases in the series [14]:



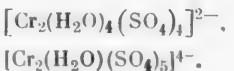
Thus, Librelich observed that in the electrolysis of a solution of chromic anhydride an intermediate pale electrolyte layer is formed near the cathode (Librelich believed it to be sulfuric acid). We carried out visual observations of the cathode space, and the electrolyte in the immediate vicinity of the cathode was also analyzed. The experiments were performed in a U-shaped tube with the cathode placed horizontally in one branch of the cell. The electrolyte was a solution containing 200 g of CrO_3 per liter, free from trivalent chromium at the start of electrolysis.

Direct observations during electrolysis showed that after the current is switched on ($i_c = 20$ amps/dm²) the electrolyte darkens near the cathode. The dark part of the solution then gradually moves away from the cathode toward the anode, and after some time a sharp boundary is formed, at a certain distance from the cathode surface, between a pale yellow solution in direct contact with the cathode and the dark part of the electrolyte. The height of the column of pale yellow solution was about 5 mm, and the height of the dark part of the electrolyte did not exceed 10 mm.

At a certain instant during the electrolysis the dark part of the electrolyte approached the electrode very rapidly and became decolorized; if the cathode was removed from the electrolyte at this instant it was found to be covered with a visible dark film which was easily soluble both in hot hydrochloric acid and in alkali.

Analysis of the solution in direct contact with the cathode, by precipitation chromatography (with the use of silver salts), showed the catholyte to contain $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions, the latter being considerably predominant.

Since the dark part of the electrolyte, containing complexes of trivalent chromium with SO_4^{2-} ions, moved toward the anode, it may be assumed that chromosulfuric acids are formed in the electrolyte; these are readily soluble in water and yield anions of the type:



Since the anode is usually at some distance from the cathode, while the diffusion rate of large complex ions is relatively very low, as electrolysis proceeds trivalent chromium accumulates at the cathode in excess relative to the amount of sulfuric acid present, and under these conditions the formation of the complex anions observed and described by Kasper [5] becomes possible; this evidently accounts for the return motion of the dark part of the electrolyte toward the cathode.

Since the presence of considerable amounts of trivalent chromium in the cathode space leads to difficulties in the electrolysis of chromate solutions, it is desirable for a normal course of the process to have the complex chromium compound predominantly in the anionic form, so that it should migrate toward the anode, where trivalent chromium is oxidized to sexivalent.

It should be noted in conclusion that a slight excess of Cr^{3+} over the sulfate ion content is useful for the production of bright chromium coatings (but not for the deposition of chromium in general), i.e., for regulation of crystal growth [15]. Chromium hydroxide which is not bound in the chromosulfate complex has surface-active properties, and is adsorbed along with other complex particles on the active regions of the growing crystals, retarding their growth. Thus, the colloidal suspension favors formation of especially microcrystalline dense deposits. The content of trivalent chromium in the electrolyte is influenced by the CrO_3 concentration; the higher the latter, the more rapid is the accumulation of Cr^{3+} ions, and it is really because of this that a perfectly definite ratio of CrO_3 and SO_4^{2-} must be maintained.

From the foregoing data and the results of direct and prolonged observations of the performance of chrome baths in industrial conditions it may be concluded that it is more important to regulate the $\frac{[\text{CrO}_3]}{[\text{SO}_4^{2-}]}$ ratio rather than the $\frac{[\text{CrO}_3]}{[\text{SO}_4^{2-}]}$ ratio, as the role of SO_4^{2-} ions reduces to elimination the harmful effect of trivalent chromium. Such regulation completely eliminates the difficulties which frequently occur in chrome

plating. The structure given above for the complex ions indicate that the $\frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{SO}_4^{2-}]}$ ratio should be roughly 1 : 2-2.5.

SUMMARY

1. In a study of the influence of sulfate ions on the electrodeposition of chromium it was shown that the action of sulfate anions in chromium plating depends on their ability to form stable and readily soluble complexes with trivalent chromium ions.
2. Complex chromosulfate ions are negatively charged and move toward the anode in electrolysis.
3. A small excess of trivalent chromium results in formation of chromium hydroxide and basic salts which, because of their colloidal character, favor the formation of bright and microcrystalline chromium deposits.
4. It is shown that in order to prevent the harmful effect of trivalent chromium the ratio $\frac{\text{Cr}_2\text{O}_7^{2-}}{\text{SO}_4^{2-}}$ in the electrolyte should be regulated close to 0.5.

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THE POSSIBILITY OF CARBON DETERMINATION IN THE CONVERTER PROCESS BY THE ELECTROMOTIVE-FORCE METHOD

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In the conversion of pig iron, which takes a short time, the burning of carbon is usually the determining process. The existing methods of rapid analysis [1-5] are still far from perfect, so that the production of steel of required composition is difficult. In the present investigation an attempt was made to apply the electromotive force method for observing variations of the carbon content during the blowing process directly in the liquid metal.

EXPERIMENTAL

Carbon may be determined in the converter process with the aid of the galvanic cell



used earlier [6] for determination of the activity of carbon dissolved in liquid iron. It is merely necessary to design it in such a way that the blown metal is the electrode of variable carbon concentration, while the reference

electrode is graphite separated from the other electrode by a layer of slag. Then, by measurement of the electromotive force the C content (in %) during the process can be determined with the aid of an appropriate calibration curve.

Preliminary experiments, performed by Gavrilov [7] in a 50 kg converter, gave encouraging results. The electromotive force increased more or less regularly with decrease of carbon content. However, certain difficulties arose in connection with the use of a liquid electrolyte and graphite leads. To avoid these difficulties, we replaced the graphite leads by tungsten, and liquid slag by solid. It may be noted that a number of workers used galvanic cells with solid glass electrolytes for determinations of the activities of fusible metals [8] and obtained relatively consistent and reproducible results.

For determination of the calibration curves, a cell 2 made from a mixture of fused magnesia powder, technical calcium carbide, and boric acid binder (60 : 50 : 5) was molded in the graphite tube 1 of a carbon resistance furnace (Fig. 1). The cell was sintered at 1400-1450°, and served as the solid electrolyte. The compartment 3 of the cell contained pig iron saturated with carbon, and the other compartment (4) contained metal with variable C content. The tungsten leads 5 were protected by porcelain tubes 6. The graphite rod 7 was immersed in the metal 3 in order to maintain a constant C concentration in it, and to measure the thermal emf between tungsten and carbon in this cell, i.e.,

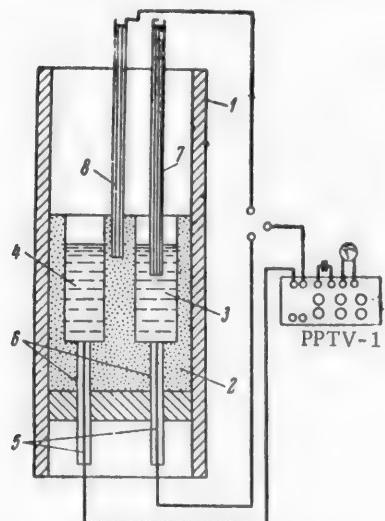


Fig. 1. Cell with solid slag, for determination of the calibration curve.

tungsten leads 5 were protected by porcelain tubes 6. The graphite rod 7 was immersed in the metal 3 in order to maintain a constant C concentration in it, and to measure the thermal emf between tungsten and carbon in this cell, i.e.,



(a)

The second graphite rod 8 was in contact with the solid slag 2 and was used as the reference electrode in the cell with the metal 4 containing a variable concentration of carbon:



(b)

Finally, the cell could be used for measurement of the electromotive force of the third cell, namely



(c)

Figure 1 also shows the electrical circuit with the PPTV-1 potentiometer. The temperature was measured by means of a W-Mo thermocouple and checked by an optical pyrometer.

The equations for the electrochemical component of the electromotive forces (E) of cells (b) and (c) are of the same form [6]:

$$E = \frac{RT}{nF} \ln \frac{a_C^0}{a_C}, \quad (1)$$

where a_C and a_C^0 are the activities of carbon in iron and in the reference electrode, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and n is the number of electrons in the equation for the potential-determining process.

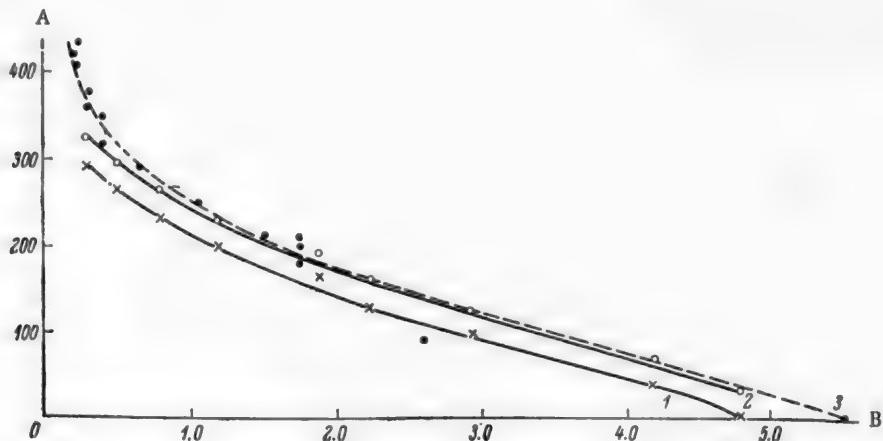


Fig. 2. Effect of carbon concentration of liquid iron on the electromotive force of Cells (b) and (c): A) emf E (mv), B) carbon concentration (%); 1) for solid electrolyte, Cell (c), 2) the same, with thermoelectromotive force, Cell (b), 3) for liquid slag [6].

Since the carbon concentration in the iron 3 is close to saturation, its activity is approximately equal to that of the graphite rod 8, and can be equated to unity, i.e., $a_C^0 = 1$. The second electrode 4 is common to both cells, and therefore they should have the same value of E . The difference between the actual values of emf is due to the thermoelectromotive force which arises between W and C in Cell (b), and which is measured separately in Cell (a), i.e.,

$$E_b - E_a = E_c. \quad (2)$$

The results obtained at 1470-1500° are given in the table and plotted in Fig. 2. The figure shows that E_c (Curve 1) varies regularly with the carbon content, and this curve lies somewhat below Curve 3, determined earlier

[6] at 1600-1630°. The thermoelectromotive forces determined directly in Cell (a) are similar to those calculated as the difference of E_b and E_c , and lie in the range of 20-27 mv.

Electromotive Forces of Cells (a), (b), and (c) for Different Carbon Contents

t (in °C)	C (%)	E_c (mv)	E_b (mv)	E_a (mv)		t (in °C)	C (%)	E_c (mv)	E_b (mv)	E_a (mv)	
				$E_b - E_c$	measured					$E_b - E_c$	measured
1470	4.2	35	62	27	20	1480	1.2	198	225	27	20
1475	2.9	98	122	24	20	1500	0.8	235	260	25	21
1470	2.2	130	155	25	20	1500	0.5	260	285	25	22
1480	1.9	160	183	23	22	1500	0.4	290	315	25	22

In determinations of carbon concentration by means of Cell (b) it is necessary to use values of E_b which include thermoelectromotive forces. The appropriate calibration curve (Curve 2) is shown in Fig. 2.

DISCUSSION OF RESULTS

In the first six experiments a small induction furnace (1.5 kg) was used for the carbon determinations. In its bottom was molded a magnesite tube with a tungsten wire lead which was in contact with blown synthetic pig iron. The metal surface was covered with calcium carbide, which contained the second electrode, a graphite rod. At about 10 cm from the melt surface there was a porcelain tube ($d = 5$ mm) through which air was blown at 4.5-5 liters/minute.

The results of the two most successful experiments are given in Fig. 3. The upper curves represent variations of electromotive force with time. The dash lines represent values of E_b found by direct measurement, and the continuous lines correspond to values calculated from the calibration curve and from the C contents by chemical analysis. To allow for temperature variations of the metal during the blow, emf isotherms were first plotted for different temperatures, and a calibration polytherm was constructed from them. The two lower curves in Fig. 3 show the carbon contents during the process, found by chemical analysis (continuous lines) and from the measured electromotive forces (dash lines) with the aid of the calibration curve.

Comparison of these results shows that the largest discrepancies are found at the initial stage of the smelting, after which the carbon concentrations determined by the emf method and by chemical analysis converge. It must be pointed out, however, that in a number of experiments there were considerable discrepancies the causes of which could not be determined.

Fig. 3. Variation of the content of carbon dissolved in liquid iron during blowing of the metal in an induction furnace: A) emf E (mv); B) carbon concentration (%); C) time (minutes); 1) change of emf, 2) emf calculated from the carbon content and from the calibration curve, 3) C content (%) by chemical analysis, 4) C content (%) from emf values.

magnesium oxide, calcium carbide, and boric acid, of the composition given earlier, was pressed in iron tubes 1 cm in diameter and 14-15 cm long, and then sintered at about 800°. The briquets so formed (1, Fig. 4) were connected to the graphite electrode 2 by means of a socket joint. When the converter was lined, special cavities were made on diametrically opposite sides of the wall in the joint between the bottom 3 and the cylindrical

For experiments in a 50 kg converter, a mixture of

portion 4. One cavity contained the solid electrolyte 1 with the graphite electrode 2, and the other a magnesite tube 5 with a tungsten lead 6. Pig iron, containing 4-4.6% C, 0.012-0.03% Si, traces of Mn (0.2%), S (0.02-0.05%), P (0.05-0.06%), was melted in an induction furnace and then poured into the preheated converter. Its temperature was not measured during the blowing.

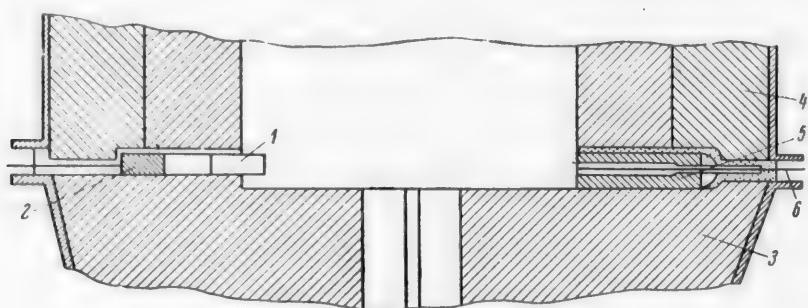


Fig. 4. Arrangement of electrodes in the converter.

The results of two experiments are given in Fig. 5. The upper curves represent the values of the measured electromotive forces, while one of each pair of lower curves (continuous lines) gives the carbon concentrations calculated from the emf by means of the calibration graph (isotherm). The lower dash lines give the results of chemical analysis. Here, as in the previous instance, there is a certain correlation between the carbon contents found by the two methods. At the same time, there are also considerable discrepancies, which are partly due to the presence of impurities (Si, Mn, S, P, etc.) in the iron, which influence the activity of carbon, and to temperature variations of the blown metal.

Thus, with the aid of the apparatus described here the emf method can give only a rough qualitative indication of variations of carbon content in the blown metal. However, these experiments gave encouraging results and it is hoped that with further improvement of the method it will become suitable for more accurate determination of the carbon content during the converter process.

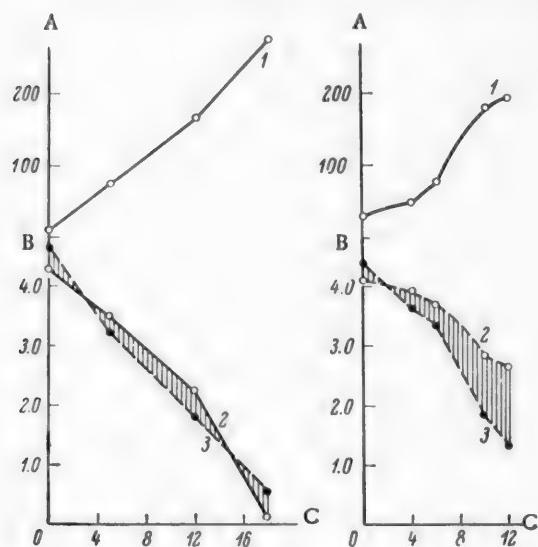


Fig. 5. Carbon content of converter metal:
A) emf E (mv); B) carbon concentration (%);
C) time (minutes); 1) measured emf, 2)
carbon concentrations calculated from emf,
3) C contents (%) by chemical analysis.

SUMMARY

1. In order to test the applicability of the electromotive-force method for carbon determination in the converter process, the galvanic cell designed

earlier for activity determinations has been redesigned so that the blown pig iron acts as the electrode of variable carbon concentration, the reference electrode is graphite, and the electrolyte is solid slag.

2. Calibration curves were plotted, giving the relationship between the electromotive forces of concentration cells with solid electrolyte and the carbon content of liquid iron. These curves were found to be analogous to those obtained previously with melted slag. The corrections for thermoelectromotive forces between graphite and tungsten leads were estimated by two methods.

3. Experiments in a 50 kg converter show that the electromotive-force method gives promising results, but in its present form can only give a qualitative idea of changes in the carbon content of the blown metal.

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SOME PROPERTIES OF ELECTROLYTIC COPPER DEPOSITS FORMED FROM ACID ELECTROLYTES BY MEANS OF PERIODICALLY REVERSED CURRENT

V. V. Ostroumov and I. F. Plotnikova

In the previous communications we considered the conditions for formation of bright copper deposits and the influence of chloride ions in the electrolyte on the reflecting power of deposits formed by electrolysis with periodically reversed current [1, 2]. This paper contains the results of a study of the structure and certain other properties of copper deposits formed under the same conditions.

Metallographic sections of the copper deposits were made by the method generally used for this purpose. To obtain a correct surface on the cross section, the deposit was previously covered with a protective layer of electrolytic copper, of arbitrary thickness. The section was polished and then etched for 1-2 seconds in concentrated nitric acid.

The composition of the electrolyte used was 200 g of copper sulfate and 100 g of sulfuric acid per liter. The solution was stirred during electrolysis. The original electrolyte was boiled with metallic copper to remove impurities.

The hardness of the deposits was found from the size of the indentation formed by a 4-sided diamond pyramid with 136° vertex angle. The Hanemann attachment (model D 30) for the large horizontal metallographic microscope was used. The measurements were performed only on layers 100 μ thick, with which the influence of the hardness of the underlayer on the final results could be disregarded. Imprints of equal diagonal length were used for hardness comparisons of different deposits.

RESULTS

Copper deposits formed on polished brass surfaces by means of direct current (80 ma/cm^2) have the usual well-defined crystalline structure (Fig. 1, a). Within the deposit it is possible to see the start of conical growths which increase the surface roughness of the coating.

Deposits formed on polished brass at the same current density but with periodically reversed current have an ordered structure (Fig. 1, b). The deposit consists of fibrous crystallites oriented at somewhat differing angles to the electrode plane. The external surface of the deposit is more level than in the first case, but is still fairly rough and scatters light strongly. The deposits are therefore dull in appearance.

The electrolysis conditions are such that copper is deposited on the electrode in layers in the second case. However, a layer structure parallel to the electrode surface could not be detected in the cross sections. This indicates that each consecutive copper layer continues the structure of the layer below it. The presence of extremely thin oxide films formed on the copper during the brief anodic pulses cannot be detected.

Copper layers deposited on bright nickel over the brass have some characteristic peculiarities.

The first layers of copper deposited by direct current contain crystallites which have distinct orientation perpendicular to the electrode plane (Fig. 2, a). However, after the copper thickness has exceeded 5-10 μ , this initial crystallite orientation breaks down and the deposit then assumes the structure typical for copper deposited directly on brass. The layers of copper deposited by periodically reversed current have a particularly ordered, and an even more microcrystalline fibrous structure (Fig. 2, b). The fibers forming the deposit have a strictly

perpendicular orientation relative to the electrode plane. The external surface of the layer is mirrorlike and has high reflectance (80-82 % for white light). No layer structure parallel to the electrode surface can be detected in this case either.

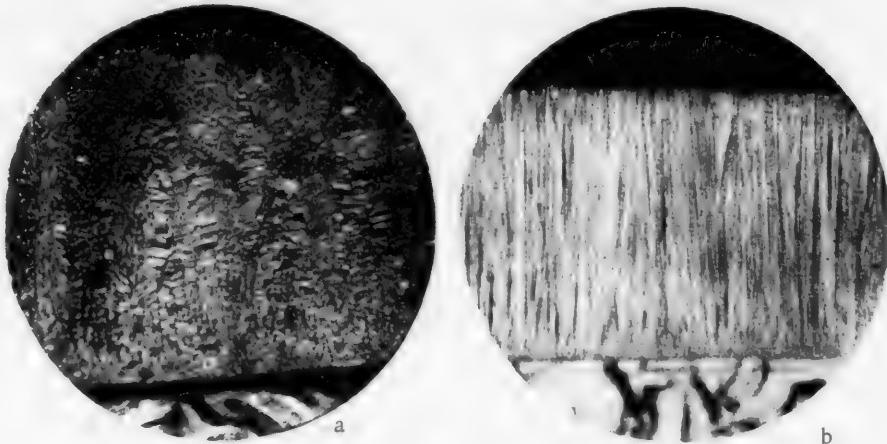


Fig. 1. Structure of copper deposited on brass. Current density 80 ma/cm^2 , $t = 20^\circ$, stirred electrolyte, magnification 400; electrolysis with a) direct current, b) periodically reversed current.



Fig. 2. Structure of copper deposited on brass with a bright nickel underlayer. Current density 80 ma/cm^2 , $t = 20^\circ$, stirred electrolyte, magnification 400; electrolysis with a) direct current, b) periodically reversed current.

Structure studies therefore reveal the orienting influence of bright nickel underlayers on the growth of copper crystallites, and show that periodically reversed current has an independent orienting effect (Fig. 1, b). We are inclined to attribute this last effect to the formation of oxide films on the copper, which appear during the anodic current pulses, and which separate the cathodic copper deposits. These interlayers help in preserving the orientation of the copper crystallites which is determined by the bright nickel surface.

It is interesting to note that when copper is deposited by means of direct current on a polished surface of a copper layer which was itself formed by electrolysis with periodically reversed current, the crystallites again exhibit orientation which continues the structure of the underlayer to a depth of $5\text{-}10 \mu$ (Fig. 3). The copper was deposited from the same bath and at the same current density (80 ma/cm^2) in both cases.

The deposits described above were prepared from an electrolyte which had been boiled with metallic copper for purification. As was stated earlier, addition of chloride ions to such an electrolyte up to concentrations of 10-20 mg/liter disturbs the formation of bright deposits. Pyramidal projections appear on the deposit surfaces, favoring light scattering and conferring a dull appearance to the deposits. Cross sections of such deposits reveal the presence, within the depth of the layers, of regions from which larger crystallites begin to grow and terminate in pyramidal projections in the surface (Fig. 4). It is interesting to note that such crystallites show a layer structure parallel to the electrode surface.



Fig. 3. Orienting influence of bright copper. Current density 80 ma/cm^2 , $t = 20^\circ$, magnification 400; below—underlayer of bright copper; above—layer of copper deposited by direct current.

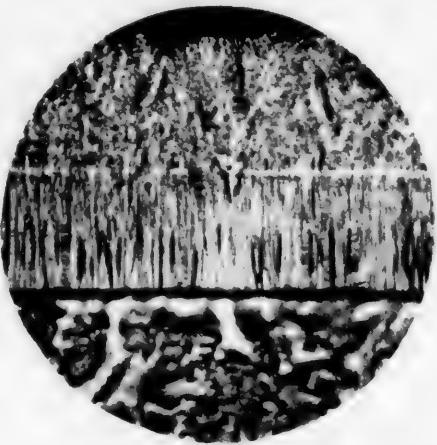


Fig. 4. Structure of a copper deposit formed in presence of 10 mg of chloride ions per liter. Periodically reversed current, current density 80 ma/cm^2 , $t = 20^\circ$, magnification 200; above—basis metal, middle—tested copper layer, below—protective layer.

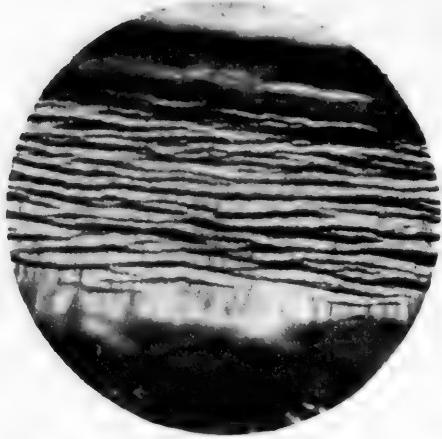


Fig. 5. Etched surface of a bright copper deposit in an oblique section; magnification 600.

The picture seen after the outer surface of the bright copper deposit had been etched with nitric acid did not indicate that the layers are composed of fine fibers. However, sections cut at an angle of 45° to the external plane of the deposit and etched with nitric acid clearly showed a step structure which indicated that the metal layers had a fibrous and extremely microcrystalline structure (Fig. 5).

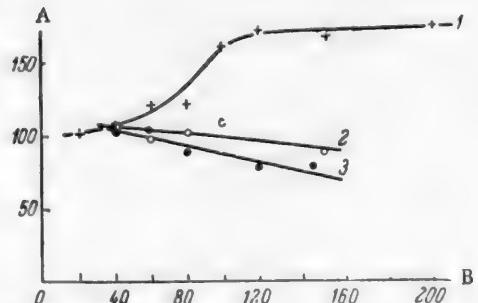


Fig. 6. Variations of deposit hardness with current density. A) Hardness (kg/mm^2); B) current density (ma/cm^2); electrolysis with: 1) direct current, $t = 20^\circ$; 2) periodically reversed current, $t = 20^\circ$ and 40° ; 3) periodically reversed current, $t = 5^\circ$.

Hardness tests on the copper deposits revealed the following characteristics (Fig. 6).*

Layers formed by electrolysis with direct current showed a hardness increase from 100 kg/mm² (at current density 20 ma/cm²) to 180 kg/mm² (at 200 ma/cm²). This kind of hardness increase has been repeatedly reported in the literature. It corresponds to decrease in the size of the metal crystallites with increasing current density.

Copper deposits formed by electrolysis with periodically reversed current do not show any appreciable changes of hardness at the same current densities and under the same experimental conditions. The results even reveal some tendency for the hardness to decrease with increase of current density. Change of the electrolyte composition from 5 to 40° had little effect on hardness; the hardness was also the same whether the electrolyte was stirred during electrolysis or not. These last results, however, are valid only for bright copper deposits.

The hardness of the bright copper deposits is evidently constant because of the constant type of structure of these deposits, as far as can be judged from microscopic observations.

In conclusion, it should be pointed out that it is claimed in certain publications that deposits obtained by electrolysis with periodically reversed current are more uniform in thickness than deposits formed by electrolysis with direct current. In our experiments the copper layers on flat cathodes were thicker at the electrode edges, the thickening being of similar extent to that found in ordinary copper deposits. Therefore, supplementary cathodes and shielding devices are necessary for the production of layers of uniform thickness over the whole electrode surface.

SUMMARY

1. The microstructure of copper deposits formed from acid electrolytes by means of periodically reversed current was studied, and it was shown that bright copper deposits have a fine fibrous structure composed of crystallites in strict perpendicular orientation relative to the electrode surface.

2. An underlayer of bright nickel can cause orientation of the crystallites in the copper deposit to a depth of 5-10 μ in electrolysis by direct current. In electrolysis with periodically reversed current this initial orientation favors the formation of a fibrous structure which spreads right through the thickness of the layer. Such layers retain a specular external surface, with high reflecting power, throughout electrolysis.

3. The presence of excess of chloride ions in the electrolyte causes the formation of large crystallites within the deposit; these terminate at the surface in pyramidal projections which disturb the specular nature of the surface.

4. The hardness of bright copper layers deposited by periodically reversed current is fairly constant; it is almost independent of current density, electrolyte temperature, and stirring conditions, and is close to 100 kg/mm². The hardness is constant because of the constant structure of the deposit.

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Received April 1, 1957

* Deposits with rough outer surfaces were ground and polished on cloth with State Optical Institute paste before the tests. The diamond pyramid was pressed into the deposits at right angles to the electrode plane.

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CATHODIC DEPOSITION OF CHROMIUM FROM POLYCHROMATE SOLUTIONS MADE BY PREVIOUS ELECTROLYSIS OF SODIUM DICHROMATE

S. S. Savel'ev and A. I. Levin

The technical process for the production of chromic anhydride used for chrome plating is based on the reaction of dichromate with concentrated sulfuric acid according to the equation



Despite its relative simplicity, this process has important disadvantages: instead of a valuable product, alkali, it yields sodium bisulfate, which is of little value and separation of which leads to losses and contamination of chromic anhydride [1]. In this paper we consider an electrochemical method for production of polychromate solutions, suitable for subsequent extraction of metallic chromium, which is free from these disadvantages.

It was shown earlier [2] that in the electrolysis of chromate solutions the greatest concentration changes take place in the layers near the electrodes.

Thus, the equilibrium which becomes established in absence of current



is shifted to the right with decrease of pH and with increase of solution concentration. With such solutions, the most probable anodic reaction at a given current density is conversion of sodium dichromate into polychromates (solutions containing free dichromic acid $\text{H}_2\text{Cr}_2\text{O}_7$ and sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$).

The experiments were performed in a cell with a mercury cathode and a lead anode (Fig. 1). The anode and cathode spaces were separated by a porcelain diaphragm which was filled with the original $\text{Na}_2\text{Cr}_2\text{O}_7$ solution. The mercury cathode was covered with distilled water where decomposition of sodium amalgam was expected to occur.

However, it was found in practice that a considerable proportion was decomposed at the diaphragm itself, so that the diaphragm surface became alkaline on the mercury (cathode) side, and part of the alkali was carried out into the decomposition liquid (catholyte) together with hydrogen bubbles.

Fig. 1. Design of an electrolytic cell with a mercury cathode and a vertical porcelain diaphragm.
1) Anolyte; 2) catholyte; 3) rubber ring; 4) iron body; 5) mercury.

The anolyte containing $\text{H}_2\text{Cr}_2\text{O}_7$ mixed with $\text{Na}_2\text{Cr}_2\text{O}_7$ was investigated by the potentiometric method [3], which was somewhat modified for simplicity and to reduce the time of analysis.

The PbO_2 indicator electrode was prepared by consecutive electrodeposition of lead and PbO_2 from alkaline plumbate solution onto platinum [4]. Electrodes prepared in this way proved to be more durable and reliable than platinum coated with PbO_2 without a lead underlayer.

The storage battery A and the voltage divider D were used to determine the current strength in the circuit consisting of the indicator (PbO_2) and calomel electrodes (Fig. 2). With polarity reversal during titration taken into account, the galvanometer scale could be utilized more fully (in both directions). The reproducibility of

the experiments was quite satisfactory, which was largely due to accurate measurement of the alkali used for titration of the electrolyte samples taken for analysis.

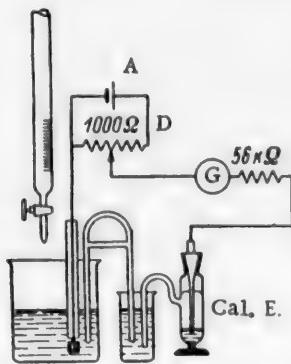


Fig. 2. Schematic diagram of amperometric titration.

To shorten the time of analysis, the titrated solution was stirred continuously. The time required to reach equilibrium at the equivalence point generally did not exceed two minutes. This improved reproducibility considerably.

Back titrations of sodium chromate by 0.1 N sulfuric acid were performed relatively rarely, and did not differ in principle from direct titration by alkali.

To determine the effect of concentration of the original solution on the current efficiency for CrO_3 , the following electrolysis conditions were tried: $t = 30^\circ$, $i_a = 6 \text{ amp/dm}^2$, $i_c = 0.71 \text{ amp/dm}^2$, electrolysis time 1 hour. An attempt to raise the current density to $i_c = 1 \text{ amp/dm}^2$ was unsuccessful, as a considerable part of the amalgam was retained in the narrow part of the cell because of the absence of stirring, and did not float up into the decomposition solution.

It follows from Table 1 that under the given electrolysis conditions the current efficiency for CrO_3 increases with the initial concentration of sodium dichromate, and reaches a maximum at a concentration close to saturation.

TABLE 1
Effect of Initial Concentration of $Na_2Cr_2O_7$ on Current Efficiency for CrO_3

Dichromate concentration (g/liter)	CrO_3 conc. at end of electrolysis (g/liter)	Current efficiency for CrO_3 (%) *	Loss of H_2O from anolyte (cc)	Amt. of water decomposed (% of initial volume)
50	37.5	22.5	14.0	56.0
100	40.0	31.2	9.0	36.0
200	42.5	40.6	8.0	32.0
300	43.5	48.6	7.0	28.0
400	45.0	55.9	6.5	26.0
500	47.5	55.8	5.8	23.2
600	53.0	63.0	5.5	22.0
700	55.9	66.0	4.8	19.2
800	60.8	67.4	4.8	19.2
900	53.2	69.5	4.6	18.4
1000	53.0	70.9	4.6	18.4
1140	58.5	74.4	4.5	18.0
Saturation at $t = 30^\circ$	64.0	76.0	4.5	18.0

* Calculated from the equivalent of $H_2Cr_2O_7$ and the CrO_3 content, with the stoichiometric amount of water disregarded.

Determinations of the amount of water lost from the anolyte owing to decomposition also confirmed that the optimum electrolysis conditions are in the region of the highest dichromate concentrations. This condition may be satisfied by increase of the electrolyte temperature.

Table 2 shows that the current efficiency for CrO_3 decreases with increase of the electrolysis time of sodium dichromate.

In individual experiments, the CrO_3 concentration under the usual electrolysis conditions reached 800 g/liter after a longer time (over 15 minutes), with a residual sodium dichromate concentration of 340 g/liter. The total current efficiency for CrO_3 did not exceed 20%, and the amount of water decomposed in the anolyte reached 80%.

TABLE 2
Effect of Time on the Current Efficiency for CrO_3 at
 $I_a = 6 \text{ amps/dm}^2$, $I_c = 0.71 \text{ amp/dm}^2$, $t = 30^\circ$ and
Initial $\text{Na}_2\text{Cr}_2\text{O}_7$ Concentration 500 g/liter

Electrolysis time (hours)	Current efficiency for CrO_3 (%)	CrO_3 concentration at end of electrolysis (g/liter)	Decomposition of water in anolyte (%)
5	35.8	275	66.0
7	25.48	320	73.2
15	19.7	480	73.2

For determinations of pH variations during electrolysis, mixtures were used in which the initial $\text{Na}_2\text{Cr}_2\text{O}_7$ solution (500 g/liter) was progressively enriched with $\text{H}_2\text{Cr}_2\text{O}_7$ until a solution was obtained containing only dichromic acid at a concentration of 415.03 g/liter.

The anolyte pH was measured by means of a glass electrode, by a method described previously [2]. The pH of the anode space was determined in the cell itself. The external current was switched off at the instant of pH determination. The determinations showed that the pH of the mixtures changes from +3.9 in 100% $\text{Na}_2\text{Cr}_2\text{O}_7$ solution to values close to zero in a solution containing 10% $\text{H}_2\text{Cr}_2\text{O}_7$.

At the same time as the pH determinations, the anode potential φ_a and the potential of the inner surface of the porcelain diaphragm φ_d were determined (Table 3).

TABLE 3
Variations of Potentials of the Anode φ_a and Diaphragm Surface φ_d With Time

Time (min)	Without current	15	30	45	60	75	90
φ_a (v)	0.925	2.188	2.168	2.148	2.148	2.138	2.138
φ_d (v)	—	1.177	0.935	0.881	0.881	0.881	0.881
E_V (v)	—	6.2	5.35	5.1	4.9	4.85	4.75
CrO_3 concentration (g/liter)	0	10	25	45	55	62	67

It follows from Table 3 that the potentials of the anode and the inner surface of the porcelain diaphragm decrease somewhat (become more negative) with increase of the dichromic-acid concentration. The voltage at the cell terminals (E_V) also decreases.

A similar change of voltage at the cell contacts was also observed with changes in the concentration of the original sodium dichromate solutions.

Further measurements of the potentials of the inner and outer surfaces of the porcelain diaphragm, with simultaneous qualitative analyses of the electrolytes, showed that the surface of the diaphragm in contact with the mercury cathode is saturated with concentrated alkali solution (without visible traces of chromate) while the inner surface, in contact with the anolyte, contains dichromic acid.

Analysis of the solutions extracted from the diaphragm pores showed them to contain sodium dichromate with various amounts of chromate. It was concluded that if solutions rich in dichromic acid are continuously removed from the cell, say by the use of a perforated lead anode, it might be possible to use diaphragm materials which are less resistant to the oxidizing action of dichromic acid.

Experiments were therefore carried out with the use of diaphragms consisting of plates of Artik tuff (4 mm thick). The mercury was covered with distilled water for decomposition of the sodium amalgam formed during electrolysis. A lead anode 6.5 cm² in area was again used. The diaphragm area was 5.3 cm². The electrolysis conditions were: $i_a = 3 \text{ amps/dm}^2$, $E = 5.5 \text{ v}$, $t = 39^\circ$ (without thermostatic control). The mercury was not stirred.

In the course of 7 hours of electrolysis the sodium dichromate was found to fall from 733.6 to 325 g/liter. The results of this experiment do not differ in principle from the results of electrolysis with a vertical porcelain diaphragm. It was also found that under certain conditions electrolysis stops almost completely: the current strength falls to 10-15 ma, while the voltage at the cell terminals rises to a maximum. The cause of this effect is evidently passivation of the surface of the mercury cathode by sodium dichromate which penetrates through the pores in the diaphragm.

Further attempts to obtain solutions rich in dichromic acid were made in experiments on electrolysis of sodium dichromate between two diaphragms of Artik tuff. The anolyte was dichromic acid, so that as it became enriched with chromic anhydride the latter could be removed from the cathode compartment, and the lost anolyte replaced either by water added from outside, or from the intermediate solution.

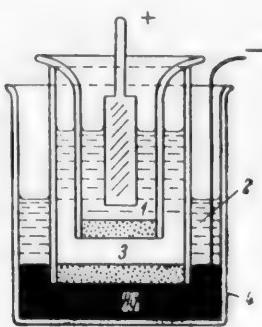


Fig. 3. Design of cell with a mercury cathode and two diaphragms. 1) Anolyte; 2) catholyte; 3) intermediate solution; 4) mercury.

and sodium dichromate (CrO_3 480 g/liter and $\text{Na}_2\text{Cr}_2\text{O}_7$ 642 g/liter) was tested in order to find whether a cathodic deposit of metallic chromium could be obtained from it. Compact chromium deposits were obtained on copper at various current densities (from 30 to 70 amps/dm²), 1% of H_2SO_4 on the CrO_3 content being added to the electrolyte. The chromium deposits were usually gray in color. This experiment demonstrated that it is quite possible to use polychromate solutions, made by electrolysis of sodium dichromate, for subsequent extraction of metallic chromium, also by electrolysis.

The data obtained in this investigation on concentration changes in chromate electrolytes are in good agreement with the observations of other workers [5], who found that increases of acidity and $\text{Cr}_2\text{O}_7^{2-}$ content in solution result in increased CrO_3 concentration. There can be no doubt that these shifts in the ionic equilibrium in polychromate electrolytes are inevitable at a given current density, i.e., they are the consequence of electrolysis conditions. At particularly high anodic current densities isopoly acids of the type $\text{H}_2\text{O}\cdot(\text{CrO}_3)_x$ [6] may be formed at the anode, with increase in the chromic anhydride concentration. This possibility is confirmed by the increase in the current efficiency for CrO_3 with increase of current density and of the initial concentration of sodium dichromate.

TABLE 4

Concentration Changes in the Anolyte and the Intermediate Compartment in a Cell
With Two Diaphragms

CrO ₃ concentration in anolyte (g/liter)	Initial	100	100	100	100
	Final	120	125	145	240
Composition of intermediate solution (g/liter)	Initial solution	248.9	300	500	733.6
	Final solution	CrO ₃ 35 Na ₂ Cr ₂ O ₇ 203.1	60 202.8	110 378.7	95 465.5
Current efficiency for CrO ₃ (%)	In anolyte	5.6	2.4	5.9	7.6
	In intermediate solution	45.9	23.5	32.9	14.4
	Total	51.5	25.9	38.8	22.0

SUMMARY

1. In studies of concentration changes in the anolyte of a bath composed of sodium dichromate it was found that the electrolyte pH changes from +3.9 to 0 in the course of electrolysis with increase of dichromic acid concentration.
2. Concentration changes in the anolyte layers have a very important influence on the composition and ionic equilibrium of sodium dichromate solutions.

When sodium dichromate is electrolyzed with the use of a diaphragm it is converted at the anode into dichromic acid and its analogs (polychromic acids), while the concentration of caustic soda in the catholyte increases.

3. The relationship between current efficiency for CrO₃ and the concentration of the original sodium dichromate solution and the electrolysis conditions has been determined.
4. It is shown that polychromate solutions containing sodium dichromate and free polychromic acids can be used for subsequent electrolytic production of metallic chromium.

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SULFATION MECHANISM OF LEAD STORAGE BATTERIES AND METHODS FOR ITS PREVENTION

T. I. Popova and B. N. Kabanov

There has been a considerable number of investigations dealing with the sulfation of negative plates of lead storage cells, as it is considered that many batteries become unserviceable owing to sulfation [1].

The term "sulfation" or "irreversible sulfation" is used in the literature to describe instances when discharged plates (i.e., plates covered with a layer of lead sulfate) do not become charged when the normal charging current is passed for the normal period of time.

Most authors attribute sulfation of negative storage-cell plates to growth of lead sulfate crystals or to formation of a "stable" form of these crystals, with a decrease of their solution rate [1-5]. It is assumed that dissolution of lead sulfate crystals is an intermediate stage in the charging process:



One of the authors of this paper [6] put forward an explanation of sulfation, which was attributed to adsorption of various surface-active organic substances on lead sulfate crystals, as the result of which the solution rate of the crystals is lowered. In that investigation the adsorption of various compounds on lead sulfate was determined indirectly from the increase of the cathodic polarization of the discharged plate caused by retardation of dissolution of the lead sulfate crystals by the adsorbed layer, and from the thickness increase of the protective lead sulfate layer, indicative of hindered crystallization.

The possibility of dissolution and crystallization of lead sulfate being retarded by organic substances follows from the work of Kolthoff and his associates [7] on the behavior of crystalline precipitates. They showed, in particular, that recrystallization of lead sulfate is retarded in presence of a number of organic substances. They determined the true surface of the crystals by adsorption of Methyl violet. In their opinion, the lead sulfate surface is covered by a continuous monomolecular layer of dye anions, which displace SO_4^{2-} ions from the surface layer of the lead sulfate lattice. Therefore, the observed adsorption of Methyl violet is of specific (chemical) and not of electrostatic character. They showed that in a neutral solution of the dye the specific surface of a lead sulfate precipitate is only roughly halved in 8 days; this shows that the recrystallization rate is lower than in absence of dye. The adsorbed dye completely stops recrystallization of lead sulfate in 0.01 N nitric acid solution, as adsorption of the dye increases with increase of solution acidity.

These results suggested that in presence of surface-active substances in a storage cell the dissolution of lead sulfate crystals may be retarded, and this hinders the charging process. This is consistent with the result, reported by a number of authors, that increase of the expander concentration above a certain limit results in cell sulfation. This was reported by Ritchie [8] in tests of the action of various expanders, and by Rose [9] in a paper on sulfation test methods. Certain separator materials may also lead to sulfation.

The literature contains a large number of methods for sulfation prevention. However, the effectiveness and suitability of these methods are not known with accuracy.

EXPERIMENTAL

In our studies of the sulfation mechanism of negative storage-cell plates we investigated recrystallization of lead sulfate in pure solutions of sulfuric acid, and also studied the influence of adsorption of surface-active substances on the cathodic polarization of an electrode consisting of lead and lead sulfate, and therefore on the solution rate of lead sulfate crystals.

The law governing diffusion of lead sulfate to the surface of a lead electrode is complicated by the fact that the source of the substance may be partially within the diffusion layer. Therefore, the steady diffusion rate and the magnitude of the limiting current are determined not only by the solubility of the given salt but also by the solution rate of the crystals, especially those which are contained within the diffusion layer. For the same reason the rate at which the solution is stirred has almost no effect on the limiting current in surface-coated plates (agitation is negligible within the deep pores of pasted battery plates). The solution rate of lead sulfate crystals in cathodic polarization directly influences the lead sulfate concentration at the surface of the electrode being charged, and therefore the magnitude of the electrode potential.

The following methods were used in the investigation: 1) determination of the limiting current in the reduction of lead sulfate, from cathodic current strength-potential curves [10], 2) x-ray structural and microscopic analysis of samples of discharged lead electrodes, 3) determinations of the capacity of the double layer, 4) determinations of discharge capacity under intermittent (starter) discharge conditions.

The test electrodes were negative lead storage-cell plates of the pasted type (3 mm thick) of 5, 10, and 50 cm^2 apparent surface area, made from litharge (without expander). These plates were formed and conditioned in 6 N sulfuric acid. The electrodes were charged by a cathodic current of density $4-5 \text{ ma/cm}^2$ calculated on the apparent surface. The forming and conditioning of the plates was taken to be complete when the potential

reached -0.6 v on the standard hydrogen scale. After the forming, the negative lead plates were conditioned by 8-fold charging and discharging. Discharge conditions: $10-13 \text{ ma/cm}^2$ (1-1.5 hours) to a potential of -0.2 v on the standard hydrogen scale. Charge conditions: $8-10 \text{ ma/cm}^2$ (2-3 hours) to -0.6 v .

Discharged lead plates were used for the experiments, the discharge being of the short-term type at current density 65 ma/cm^2 down to -0.2 v . The discharge capacity of the plate was determined from its discharge time.

The polarization determinations were performed in an air-tight vessel (Fig. 1) at room temperature. The lead electrode 1 was placed in the middle of the main vessel. The second (platinum) electrode 2 was contained in a tube separated from the main solution by the glass filter 3. The potential of the lead electrode was determined by the compensation method against a mercury-mercurous sulfate electrode 4, with the same acid concentration as in the main solution. The experiments were conducted in a hydrogen atmosphere.

Fig. 1. Diagram of apparatus; explanation in text.

The determinations of the cathodic polarization curves were started at low current densities, in the $2 \cdot 10^{-4}$ to $2 \cdot 10^{-1} \text{ amp/cm}^2$ range. A sharp rise of the electrode potential indicated that the limiting current for discharge of lead ions had been reached, and hydrogen liberation started. The polarization curves were determined after the electrode had been kept in the discharged state for 10 minutes, and 24, 48, and 120 hours (it was assumed that if an uncharged storage cell was kept for several days under the corresponding conditions the negative plates would undergo appreciable sulfation). In investigations of surface-active substances each negative lead plate was used in several experiments (being cleaned between the experiments) and was subjected to repeated discharging and charging (about 20-30 cycles).

After experiments with organic substances the electrode was washed in 8 N sulfuric acid to remove them, and then subjected to cathodic polarization in pure 8 N sulfuric acid for 1-2 hours at current density $80-100 \text{ ma/cm}^2$, and discharged at current density 65 ma/cm^2 down to -0.2 v to check the capacity.

The cleanliness of the cleaned electrode was checked by the cathodic limiting current in 8 N sulfuric acid. Freshly prepared lead electrodes were used immediately after the discharge-charge cycles for experiments with pure sulfuric acid solutions.

The sulfuric acid solutions were purified by polarization with smooth lead anodes for 10-15 hours with a current of 100-200 ma. The organic substances present in traces were thereby oxidized at the anode, while metallic impurities in the acid were liberated at the cathode. For determination of adsorption of various organic substances the capacity of the double layer was determined at smooth lead electrodes (SV grade) by the usual alternating-current method in the frequency range from 1000 to 50,000 cycles/second with small cathodic polarization (the electrode potential was -0.4 v on the standard hydrogen scale) in pure sulfuric acid and in presence of various surface-active substances.

The x-ray structural analyses of discharged lead electrodes were performed in N. A. Shishakov's laboratory.* For the x-ray determinations discharged electrodes were used; they were previously kept for various intervals in the appropriate solutions, washed with redistilled water to remove traces of acid, dried, and powdered.

The behavior of negative lead electrodes subjected to the action of surface-active substances was checked by determinations of their discharge capacity. In practice, the discharge capacity was taken to be the quantity of electricity required to discharge a plate at the rapid rate (at constant current density of 65 ma/cm²) down to a potential of -0.2 v.

After determination of the polarization curves the plates were charged, before determination of the discharge capacity, at current density 5-10 ma/cm² for 2-4 hours to a potential of -0.6 v. The discharge capacity of the plates used under starter conditions (at 65 ma/cm²) was then determined.

Thus, the electrodes received the normal charge only, and if the charge process was hindered the electrode remained undercharged, and the discharge capacity was largely a measure of the completeness of the charge.

RESULTS

Cathodic polarization curves (Fig. 2) determined in pure sulfuric acid solutions showed that at all the concentrations tested (6, 7, 8, and 11 N) the limiting current for discharge of lead ions is almost the same, and is approximately $2 \cdot 10^{-1}$ amp/cm².

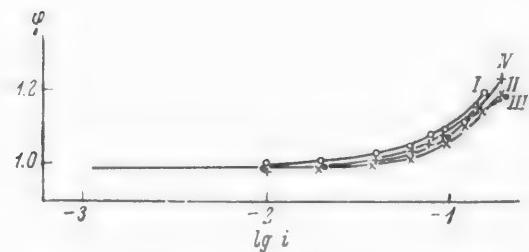


Fig. 2. Cathodic polarization curves determined after exposure of a lead electrode to H_2SO_4 solutions for 10 minutes and 15 days. H_2SO_4 concentration: I) 11 N, II) 7 N, III) 6 N, IV) 8 N.

acid, and in 8 N sulfuric acid solutions containing extracts of unwashed Mioplast (used as separator material in the storage cells), unleached pine wood, cedar and alder sawdust, etc. The results of x-ray analysis revealed the presence of numerous large crystals of lead sulfate (from 5 to 10 μ in size) on all the specimens.

Microscopic examination at 680 and 1500 magnification showed a mass of fine lead sulfate crystals, the largest being approximately 1 μ , on a discharged plate removed from the electrolyte immediately after discharge, washed, and dried. In addition to the fine crystals, crystals up to 2 μ in size were found on plates kept in the discharged state in pure electrolyte for 3 days. Increase of the exposure time of the discharged electrode to

The limiting current does not vary with time, and it is the same for discharged electrodes kept in 8 or 11 N sulfuric acid solutions for 10 minutes and for 10 or 15 days. The discharge capacity was also virtually constant. Therefore, the growth of lead sulfate crystals, which undoubtedly occurs when the discharged electrodes are left in sulfuric acid solutions, does not reduce the solution rate of the sulfate.

We studied the effect of storage of the discharged plates under different conditions on the recrystallization of lead sulfate. Different specimens of the negative plates were subjected to x-ray and microscopic analysis after exposure in the discharged state for various periods from 3 days to 5 months in 8 N solution of pure sulfuric

* We take this opportunity to express our deep gratitude to N. A. Shishakov, and also to V. P. Moiseev for the determinations and calculations.

8 days caused some lead sulfate crystals to grow to 5μ . Finally, when discharged electrodes were kept for up to 5 months in pure acid solution or in a solution containing surface-active agents, some of the lead sulfate crystals grew to 10μ .

These determinations show that the surface-active substances tested do not retard recrystallization of lead sulfate significantly.

To determine the influence of surface-active substances on the solution rate of lead sulfate, polarization curves were determined for pure sulfuric acid solution and solutions of the following organic substances in 8 N sulfuric acid: 0.001 to 0.1 M resorcinol, 0.01 M mannitol, 0.001 M Methylene blue, 0.01 M Complexon, 0.04 M sodium lignosulfonate, and extracts of humic acid, peat, wood, Miplast,* saponin, etc.

All the substances tested lowered the limiting current for the reduction of lead ions 2 to 15-fold, according to the nature of the substance and the time of exposure of the discharged electrodes to solutions of these substances in 8 N sulfuric acid, and they all lowered the discharge capacity of the plates under starter discharge conditions. If Complexon was present in the electrolyte, the hydrogen overvoltage at the lead electrode was very much decreased, and the polarization curve assumed the form of a hydrogen-overvoltage curve without any inflection indicative of a limiting current. Because of the decreased hydrogen overvoltage the negative plate did not become charged, so that the discharge capacity of the electrode fell almost to zero.

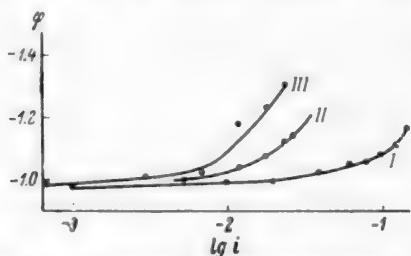


Fig. 3. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 , II) 8 N H_2SO_4 + 0.01 M mannitol (after 10 minutes), III) the same (after 24 hours).

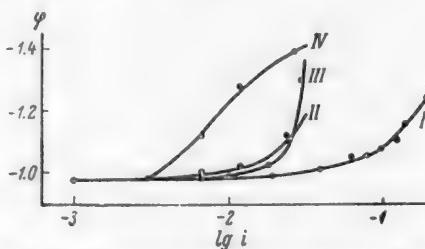


Fig. 4. Cathodic polarization curves determined for different solutions. IV) 8 N H_2SO_4 , II) 8 N H_2SO_4 + saturated solution of sodium lignosulfonate concentrate (after 10 minutes), III) the same (after 14 hours), IV) the same (after 48 hours).

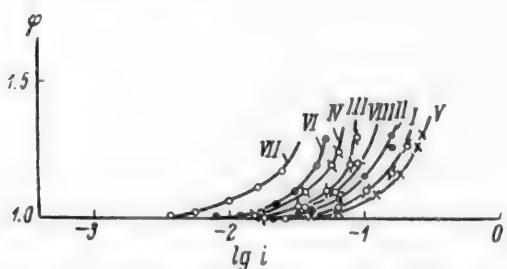


Fig. 5. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 , II) with added extract of unleached pine (after 15 minutes), III) the same (after 24 hours), IV) the same (after 48 hours), V) the same (after correction of electrode), VI) with added extracts of unleached pine and alder sawdust (after 10 minutes), VII) with added extracts of unleached pine and alder sawdust and 0.1 M resorcinol (after 1 hour), VIII) with added extracts of unleached pine and alder sawdust (after correction of electrode).

The results are illustrated by Figs. 3, 4, and 5, which give cathodic polarization curves determined after discharged electrodes had been kept for 10 minutes and 24 or 48 hours in 0.01 M mannitol solution, in saturated solution of sodium lignosulfonate concentrated, in extracts of pine wood and alder sawdust, and in 0.1 M resorcinol, all in 8 N sulfuric acid. The polarization curves show that after only 10 minutes of exposure of the discharged plates in these solutions the limiting current for the solution (the solution rate) of lead sulfate decreases. Increase of the exposure time to 1-2 days produces a 5 to 15-fold decrease of the limiting current. The discharge capacity, under brief discharge conditions, falls from 10-15 minutes to 1 minute and even to 20 seconds, which means that the electrodes are considerably sulfated.

For experimental convenience, resorcinol was used in detailed studies of the effects of surface-active substances on the charging of lead negative electrodes. According to [8], it is a model expander for negative

* It is interesting to note that extract of unwashed Miplast had a lowering effect on the limiting current and discharge capacity, whereas extract of washed Miplast had no influence on them.

lead plates on the one hand, and a substance with small molecules and good solubility in sulfuric acid on the other. Three different resorcinol concentrations, 0.001, 0.01, and 0.1 M, in 5, 6, 7, 8, 9.8, and 11 N sulfuric acid were used in studies of their effect on the limiting current of lead ion discharge and the discharge capacity of lead electrodes.

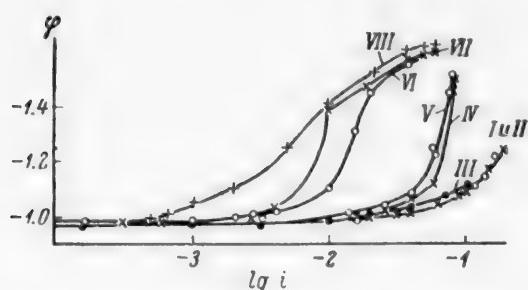


Fig. 6. Cathodic polarization curves determined for different solutions. I and II) 8 N H_2SO_4 (after 10 minutes and after 24 hours), III) 8 N $\text{H}_2\text{SO}_4 + 0.001$ M resorcinol (after 10 minutes), IV) the same (after 24 hours), V) 8 N $\text{H}_2\text{SO}_4 + 0.01$ M resorcinol (after 10 minutes), VI) the same (after 24 hours), VII) 8 N $\text{H}_2\text{SO}_4 + 0.1$ M resorcinol (after 10 minutes), VIII) the same (after 24 hours).

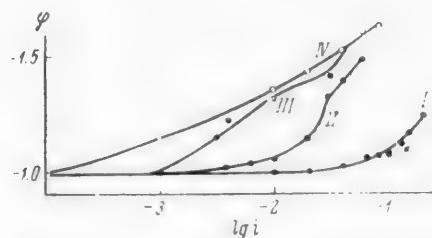


Fig. 7. Cathodic polarization curves determined for different solutions. I) 11 N H_2SO_4 (after 10 minutes and after 24 hours), II) 11 N $\text{H}_2\text{SO}_4 +$ extract of untreated wood (after 1 hour), III) the same (after 24 hours), IV) the same (after 48 hours).

polarization curves. In some cases the curves become so flat that it is difficult to determine the limiting current, and the curves become straight lines in semilogarithmic coordinates (Fig. 7, Curves III and IV). In this case, the discharge capacity falls almost to zero after 48 hours of exposure. The probable cause of this change in the form of the curve is that the overvoltage for the reduction of lead ions increases under the influence of surface-active substances.

For determination of the mechanism of action of surface-active substances on the charging of a negative lead electrode in such cases it was of interest to determine whether the action of surface-active substances is the same when charged or discharged electrodes are exposed to their solutions, i.e., with predominant adsorption on the metal or on lead sulfate, respectively.

Figure 8 shows polarization curves determined for discharged and charged lead electrodes in pure sulfuric acid solution (after "correction" of the electrode) and in a 0.001 M solution of Methylene blue in 8 N sulfuric

Figure 6 shows polarization curves determined in 8 N sulfuric acid in presence of different concentrations of resorcinol. It follows from the curves that the limiting current for solution of lead sulfate crystals depends on the resorcinol concentration in the electrolyte. With 0.001 M resorcinol the limiting current is decreased appreciably only after prolonged exposure of the electrode to the solution. The greatest decrease of limiting current (from $2 \cdot 10^{-1}$ amp/cm² to $6 \cdot 10^{-3}$ amp/cm²) is found in presence of 0.1 M resorcinol. Figure 6 shows that the retarding effect of resorcinol on dissolution of PbSO_4 increases with the time of exposure.

A small addition of resorcinol (0.001 M) increases the discharge capacity by about 50% on exposure of the discharged electrode in the electrolyte for 10 minutes and 24 hours. When the resorcinol concentration in the electrolyte was raised to 0.01-0.1 M, the discharge capacity fell from 8 to 1-2 minutes. In agreement with [8], our experiments with resorcinol showed that for each soluble expander there is an optimum concentration at which it improves the discharge characteristics of the electrode. At high concentrations the expander has the opposite effect.

With low resorcinol concentrations (0.001 M) the decrease of the limiting current of lead sulfate dissolution depends little on the sulfuric acid concentration. The sulfuric acid concentration has an effect in presence of 0.01-0.1 M resorcinol. In 5, 6, and 7 N sulfuric acid solutions addition of 0.1 M resorcinol lowers the limiting current 2 to 5-fold in comparison with the limiting current for discharge of lead ions in pure acid, while in 8, 9.8, and 11 N sulfuric acid the decrease is 20 to 40-fold. The maximum retarding effect was found in 9.8 sulfuric acid.

Certain organic substances, especially in high concentrations and with long exposure times of the discharged electrodes in the solutions, influence the form of the

acid. After exposure of a well-charged electrode for 24 hours in Methylene blue solution (Curve III, Fig. 8), the curve does not show an inflection characterizing the limiting current, and the electrode potential, starting from current density $2 \cdot 10^{-2}$ amp/cm², increases linearly with the logarithm of the current density; this is a sign of a high overvoltage for lead ion discharge. After the same length of exposure of a completely discharged electrode in the same solution of Methylene blue (Curve V, Fig. 8), on the contrary, the curve obtained has a distinct inflection, characterizing a limiting current and not an increase of overvoltage.

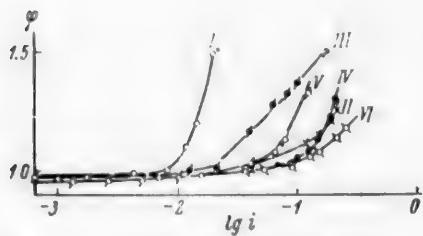


Fig. 8. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 (on sulfated electrode), II) the same (after correction of the electrode), III) 8 N $\text{H}_2\text{SO}_4 + 0.001$ M Methylene blue (after 24 hours of exposure of charged electrode), IV) the same (after correction of the electrode), V) 8 N $\text{H}_2\text{SO}_4 + 0.001$ M Methylene blue (after 24 hours of exposure of discharged electrode), VI) the same (after correction).

These experiments indicate that Methylene blue may be adsorbed both on lead sulfate crystals and on spongy lead, retarding the process in different ways.

It should be noted that a steep curve, for a very dense adsorption layer, can also be obtained if the activation energy for transport of ions through the adsorption layer on the metal is high [11]. We tested the action of a saturated solution of a mixture of β -naphthol, diphenylamine, and thymol, i.e., a mixture of surface-active substances which, according to Loshkarev [11] hinders discharge of bivalent metal ions because of adsorption of these substances in a very dense layer on the metal surface. Both charged and discharged electrodes were used for tests of the action of this mixture on the sulfation of lead plates. Figure 9 shows polarization curves for an electrode after exposure in the charged state*. In this mixture for 10

minutes and 24 hours. It is clear from the configuration and shape of the curves that brief action of a mixture of powerful surface-active agents merely raises the reduction overvoltage for lead ions (Curve II), whereas prolonged adsorption results in the appearance of a distinct limiting current (Curve III). The decrease of the limiting current may be attributed to formation of a dense adsorption film on the metallic lead.

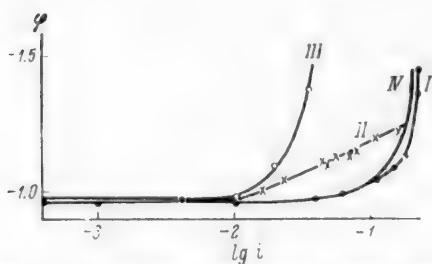


Fig. 9. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 solution, II) 8 N H_2SO_4 solution + saturated solution of a mixture of β -naphthol, thymol, and diphenylamine (after 1 hour of exposure of a charged electrode), III) the same after 24 hours of exposure of a charged electrode, IV) the same (after correction).

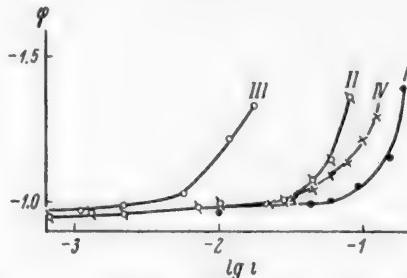


Fig. 10. Cathodic polarization curves determined for different solutions. I) 8 N H_2SO_4 solution, II) 8 N H_2SO_4 + saturated solution of a mixture of β -naphthol, thymol, and diphenylamine (after 1 hour of exposure of a discharged electrode), III) the same (after 24 hours of exposure), IV) the same (after correction of the electrode).

Figure 10 leads to the conclusion that these surface-active substances may also retard the dissolution of lead sulfate. The cathodic polarization curves in this figure were determined for an electrode exposed in the discharged

* Before the determination of the polarization curve the electrode was partially discharged in a solution of this mixture.

state for 1 and 24 hours in a saturated solution of a mixture of β -naphthol, diphenylamine, and thymol in 8 N sulfuric acid. The polarization curves show that the limiting current decreases with increase of the exposure time of a discharged electrode in this solution.

To verify the adsorbability of the substances tested on the surface of a negative lead plate, we determined the capacity of the double layer on a smooth lead electrode in pure 8 N sulfuric acid and in presence of these surface-active substances. The results of these experiments showed that addition of a mixture of β -naphthol, thymol, and diphenylamine to the electrolyte decreases the capacity of the double layer by nearly one-half at a potential of -0.4 v. Surface-active substances used in storage cells, such as humic acid extracts, wood extracts, or resorcinol, have almost no effect on the capacity of the double layer on a lead electrode. Addition of 0.01 M Methylene blue to 8 N sulfuric acid increased the capacity of the double layer at 20,000 cycles per second from $28 \mu\text{F}/\text{cm}^2$ to $39 \mu\text{F}/\text{cm}^2$. The increase of capacity may be tentatively attributed to a shift of the zero-charge potential in the negative direction owing to adsorption of Methylene blue anions. At the potential of -0.4 v at which the capacity was determined, increase of the positive surface charge could lead to increased deformation of the anions (as is known, the zero-charge potential on pure lead is -0.7 v).

In a number of cases the cell plates subjected to prolonged action of surface-active substances could not be corrected by the methods generally recommended for prevention of sulfation. For example, plates kept for 10-30 days in a solution of wood extract in 8 N H_2SO_4 did not regain their initial capacity after 6-8 hours of charging in dilute sulfuric acid. We therefore had to develop a more effective method for prevention of sulfation.

Negative lead battery plates subjected to prolonged action of surface-active substances were corrected by charging at a high current density ($100 \text{ ma}/\text{cm}^2$) for 1-2 hours in 8 N sulfuric acid. Correction of the plates may be performed even if various surface-active substances are present in solution. Examples of electrode correction are given in Figs. 5, 8, and 9, which show polarization curves for electrodes after exposure to surface-active substances, and after correction in the same electrolytes. It must be pointed out that after treatment with surface-active substances these plates could not be charged under the normal conditions (at $5 \text{ ma}/\text{cm}^2$), and the discharge capacity under starter conditions fell to zero. As the result of correction, the discharge capacity of the plates returned to the initial values, obtained in pure sulfuric acid solution. The following experimental results provide another example. Large plates were kept in the discharged state for 1-2 months in unleached pinewood extract in 11 N sulfuric acid, to which 0.1 mole of resorcinol per liter had been added. As the result of this treatment the plates could not be charged by the ordinary method, i.e., they were artificially sulfated. After being charged for 2 hours by a cathodic current at density $100 \text{ ma}/\text{cm}^2$, the plate was no longer sulfated, and the discharge capacity under starter conditions reached the initial value of $0.02 \text{ amp}\cdot\text{hr}/\text{cm}^2$.

The correction method was also tested with a small storage cell with two negative plates, of 1 dm^2 total area. The negative plates were first artificially sulfated by exposure in a separate vessel for 2 months in an extract of unleached wood and 0.1 M resorcinol in 11 N sulfuric acid, after which the plates were left without electrolyte for one month. These plates were found to be sulfated, and could not be charged under the normal conditions (at $5-10 \text{ ma}/\text{cm}^2$). After correction at high current density (current strength 8-9 amps) for 1 hour, the capacity under starter conditions reached the initial value ($0.03 \text{ amp}\cdot\text{hr}/\text{cm}^2$).

DISCUSSION OF RESULTS

It follows from literature data and our results that lead sulfate crystals grow in size as the result of recrystallization, which means that the rate of solution should decrease. Our experiments with different concentrations of pure sulfuric acid showed that the limiting current of lead ion discharge is independent of crystal size. From this it may be concluded that in absence of surface-active substances the limiting current is determined not by the solution rate of lead sulfate crystals but by the rate of diffusion of lead ions from the dissolving surface to the electrode. In fact, at limiting charging current density $i_n = \frac{2 \cdot 10^{-1}}{2000} = 10^{-4} \text{ amp}/\text{cm}^2$, calculated on the true surface (according to our data, the true surface of a charged lead electrode is 2000 times the apparent surface), with the solubility of $\text{PbSO}_4 = 3.5 \cdot 10^{-9}$ mole/cc and diffusion coefficient $D = 2 \cdot 10^{-5} \text{ cm}^2/\text{second}$, the effective thickness δ of the diffusion layer should be:

* The electrode surface, determined from the amount of adsorbed dye, was found to be $0.3 \text{ m}^2/\text{g}$.

$$\tau_{\text{d}} = \frac{n \cdot F \cdot D \cdot \Delta C}{i_n} = \frac{2 \cdot 10^5 \cdot 2 \cdot 10^{-5} \cdot 3.5 \cdot 10^{-9}}{10^{-1}} = 1.4 \cdot 10^{-1} \text{ cm}, \quad (1)$$

i.e., approximately $\frac{1}{100}$ of the thickness of the diffusion layer in a virtually unstirred liquid in absence of sources of the substance in the liquid itself. This effective thickness is roughly equal to the average distance between the surface of the lead sulfate crystals and the surface of the growing lead crystals. It is of the same order of magnitude as, or even greater than, the linear dimensions of the smallest crystals of lead sulfate which are the sources of the substance in the liquid. The certain increase in the size of these crystals which results from recrystallization of the salt in a discharged plate evidently does not cause any significant change in the distance between the growing lead crystals and the dissolving lead sulfate crystals. This distance (of the order of 1μ) is probably determined by the condition of maximum electrical conductivity and diffusion at the electrode surface, which results in directed growth of the lead dendrites toward the PbSO_4 crystals. The decrease in the solubility of the salt with increase of the acid concentration, which should decrease the limiting current [Eq. (1)] is evidently balanced by a decrease in the thickness of the diffusion layer due to increased packing density of the lead sulfate crystals on the lead. This last effect results in a decrease in the thickness of the passivating layer of lead sulfate.

Our experiments conclusively refute the usual explanation of the sulfation effect, which is based on the assumption that growth of lead sulfate crystals (due to recrystallization) retards solution of the salt so much that charging of the negative electrode becomes impossible. Our investigation confirmed the theory according to which a sharp retardation of the solution of lead sulfate (at least by a factor of some tens or hundreds) is caused by adsorption of various substances (poisons) on the lead sulfate crystals. When the limiting charging current becomes considerably less than the normal charging current as the result of poisoning, hydrogen is evolved during charging and the negative electrode remains virtually uncharged. This effect is facilitated by increase of the overvoltage of lead ion discharge, decrease of the hydrogen overvoltage (for example, by antimony, and by Complexon in our experiments), and possibly by increase of crystal size, which decreases the amount of surface-active substances required to cover the surface of all the crystals.

The fact described in the literature that after prolonged operation of a storage battery the lead sulfate crystals are larger on the positive than on the negative plate is explained, in our view, on the assumption that in the conditions prevailing on the positive plate surface-active substances are generally oxidized to water and carbon dioxide, and therefore they cannot prevent either recrystallization of lead sulfate in the discharged state or rapid solution of lead sulfate crystals during charging.

Negative plates kept for a fairly long time in solutions of surface-active substances are found to be sulfated, the limiting cathodic current on them falls sharply, reaching in many cases the value of 10^{-3} amp/cm², which corresponds to the normal thickness of the diffusion layer in absence of sources of the substance within it. This last result is possible in practice during retarded and simultaneous dissolution of the whole mass of lead sulfate crystals. The discharge capacity of such plates is low, for example, it may be 0.003 amp·hr/cm², because such plates cannot be fully charged under the usual charging conditions.

Surface-active substances cause sulfation when present in sufficient quantity in solution; for example, resorcinol in 0.01-0.1 M concentrations. At lower concentrations, such as 0.001 M, resorcinol is not a poison, as evidently it does not completely block the lead sulfate surface on adsorption, but merely retards solution somewhat and therefore acts as an expander. This accounts for the practical fact that soluble expanders have optimum effectiveness (in ensuring maximum capacity of the negative electrodes at high current densities) at a definite concentration.

In some cases an expander can be simultaneously a poison because of impurities present in it. These harmful impurities in expanders can be detected by our method for determination of the solution rate of lead sulfate from the limiting discharge current of lead ions.

Certain substances, which according to our experiments favor sulfation of negative storage-cell plates, are readily adsorbed on the surface of metallic lead (for example, a mixture of β -naphthol, thymol, and diphenylamine, and Methylene blue). This suggests that difficulties in charging negative plates after exposure to solutions of such surface-active substances may also be associated with hindered discharge of lead ions on metallic lead owing to formation of a dense adsorption layer (in accordance with M. A. Loshkarev's theory), penetration of which requires a high activation energy. In the electrodeposition of bivalent metals in presence of a mixture of diphenylamine, thymol, and β -naphthol, there is an apparent limiting current [11].

Thus, we may assume that sulfation of negative plates may be caused by adsorption of surface-active substances both on lead sulfate crystals and, in certain instances, on the surface of metallic lead. To determine the mechanism in the case of substances which are easily adsorbed both on the metal and on salt crystals, it is necessary to know how these substances are capable of spreading over solution—metal and solution—salt interfaces. In absence of surface volatility, previous adsorption of the substance on the surface of one of the phases conclusively determines the role of the retardation at this surface in the total rate balance. Apart from retardation of dissolution of lead sulfate and retarded reduction of lead ions, difficulties in charging of the negative electrode may also be caused by a decrease of the hydrogen overvoltage. This decrease is usually caused by antimony, and also by other substances such as the above-mentioned Complexon.

Our method for correction of sulfated plates by the use of high charging current densities (of the order of 100 ma/cm²) is based on the concept that sulfation proceeds by an adsorption mechanism. At these current densities the electrode potential reaches high negative values (1.2–1.4 v on the negative side of the standard hydrogen electrode, and 0.5–0.7 v on the negative side of the zero-charge potential of lead) at which surface-active substances (especially of the anionic type) are desorbed from the spongy lead surface, partially reduced, and possibly removed by flotation from the surface of the lead sulfate crystals by the liberated hydrogen. With the exception of Complexon, all the substances tested increase hydrogen overvoltage when adsorbed on the electrode surface. This is observed during reduction of sulfated electrodes: desorption of resorcinol, various extracts of humic acid, and wood during reduction of lead at constant current density is accompanied by a gradual shift of the electrode potential in the positive direction, reaching 0.2–0.4 v during the charge time (1–2 hours).

SUMMARY

1. A polarization method for determination of the solution rate of lead sulfate has been developed and used for studying the sulfation mechanism of negative plates in lead storage cells.
2. The sulfation mechanism postulated earlier by one of the authors is confirmed; according to this mechanism, the sulfation effect is due to adsorption of surface-active substances on the surface of lead sulfate crystals, hindering dissolution of the crystals.
3. It is shown that in presence of substances which are easily adsorbed on lead difficulties arise in the charging of negative plates because of shielding of the spongy lead surface.
4. It is shown that if the negative electrode remains for a long time in the discharged state in absence of surface-active substances (when the lead sulfate crystals increase in size by recrystallization), no difficulties (sulfation) arise in charging of the electrode.
5. Our method for determination of the solution rate of lead sulfate from the polarization curves and from determinations of discharge capacity can be used for analysis of organic substances used as expanders, separators, etc., for impurities which are harmful to the negative electrode.
6. A new method has been developed for correction of sulfated plates by removal of adsorbed substances by means of very strong cathodic polarization.

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DIRECT ELECTROCHEMICAL SYNTHESIS OF KO₂

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The problem of production of KO₂ without the use of metallic potassium has been the subject of several investigations [1-5]. Oxidation-reduction reactions are of great interest in relation to the formation of alkali-metal peroxides.

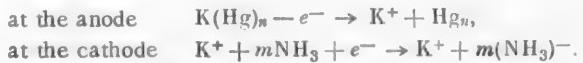
For example, hydrazobenzene is oxidized by molecular oxygen in presence of alkali-metal alcoholates with formation of the alkali-metal peroxide, alcohol, and azobenzene. The alkali-metal amalgam in presence of alcohol reduces azobenzenes to hydrazobenzene, and the latter is again oxidized together with the alkali-metal alcoholate. Thus, the oxidation-reduction process is effected continuously in a closed cycle.

Cunningham [6] reports, for example, that this continuous method can be used for production of sodium peroxide diperhydrate in 90% yield; the product can be used as a starting material for the production of sodium superoxide.

Our object was to effect direct electrochemical synthesis of KO₂. For this, potassium amalgam was subjected to anodic oxidation in a solution of potassium bromide in liquid ammonia, with simultaneous oxidation of the solution of potassium in ammonia, formed at the cathode, by molecular oxygen.

The electrochemical process for production of potassium amalgam is well understood and effectively operated. Anodic oxidation of the amalgam with simultaneous oxidation of the potassium solution at the cathode by molecular oxygen is the subject of the present study.

The electrolysis scheme may be represented as follows:



The anode process consists of extraction of the alkali metal from the amalgam present in the solution of the alkali-metal salt in ammonia. At the cathode electrons are transferred from the electrode to the solution, $\theta\text{M}^- - m(\text{NH}_3)^-$, with accumulation of the alkali-metal ions in the solution, which is equivalent to formation of a solution of the alkali metal in liquid ammonia.

Thus, the anions of the dissolved salt should play only an auxiliary role, taking part in transport of electricity; theoretically the electrolyte should not be consumed.

The solution of alkali metal in ammonia is oxidized by molecular oxygen at the instant of its formation. The potassium superoxide which is formed in the process can be retained and isolated as the end product. A necessary condition for this is that metal dissolved in ammonia should not accumulate in the reaction zone, because in presence of a solution of the alkali metal in the reaction zone the superoxide is reduced to the oxide, which reacts with ammonia to form the amide and hydroxide:



The excess metal can be removed from the reaction zone by means of a suitable method for mixing oxygen with the electrolyte.

Two types of electrolytic cells were tested, with different methods for mixing the catholyte with oxygen.

The electrolytic cell with a stirrer, shown in Fig. 1, was used for more intensive mixing of oxygen with the electrolyte. The stirrer was situated close to the cathode (platinum wire). Oxygen was led in through the tube m directly to the stirrer blades (rotating at 1500 revolutions per minute) which mixed the oxygen intensively with the electrolyte. The stirrer terminated below in a small paddle which stirred the amalgam. At the end of an experiment the amalgam was poured off through the bottom stopcock, the ammonia was evaporated off, and the residual potassium oxides were analyzed. For this 25 cc of 0.1% aqueous $\text{Co}(\text{NO}_3)_2$ solution was introduced into the electrolytic cell from a separating funnel. The oxygen evolved was collected in a Mariotte vessel filled with acidified water. The composition of the potassium oxides was found from the amount of oxygen evolved.

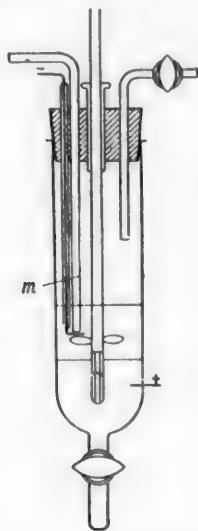


Fig. 1. Electrolytic cell with stirrer.

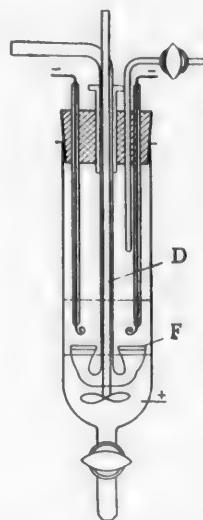


Fig. 2. Electrolytic cell without stirrer.

It was found in practice that with vigorous stirring of the electrolyte saturated with oxygen electrochemical oxidation of potassium at the cathode is accompanied by direct oxidation of the amalgam. The degree of oxidation of the amalgam by direct interaction with oxygen naturally increases with the rate at which the solution flows over the amalgam surface. This accounts for the apparent increase of the current efficiency at the anode, which reached 205% in some experiments. (This fact is in itself worthy of attention and may form the subject of a special investigation).

The electrolytic cell shown schematically in Fig. 2 was used for mixing oxygen with the catholyte without appreciable stirring of the electrolyte.

The problem was essentially to mix oxygen with the catholyte without appreciable renewal of the solution at the amalgam surface. The oxygen was dispersed by means of glass filters from 10 to 20 mm in diameter. The filters were placed at a distance of 10 mm below the cathodes (spirals).

The glass diffuser D with sealed-in filters F was immersed in the amalgam so that the edges of the glass filter projected by 10-15 mm above the amalgam surface; the distance between the electrodes was therefore roughly 25 mm.

The electrolysis was outwardly different from that in the experiment described above. First, the lower part of the electrolyte (below the glass filter) was hardly stirred at all, despite the fact that the solution was vigorously agitated in the upper portion.

At the start of electrolysis straw-yellow flakes were formed; these eventually disappeared, the solution became clear, and a pale yellow, fairly mobile precipitate of KO_2 appeared in the amalgam surface; in some experiments the layer was 10–20 mm thick. The results of the experiments are given in Table 1.

TABLE 1
Results of Experiments on Anodic Oxidation of Amalgam •

Expt. No.	Current strength (amp)	Voltage (v)	Electrolysis time (min)	Active-oxygen content of precipitate (%)			K dissolved at anode (current efficiency, %)
				calc. from current	found	found after KBr subtracted	
1	1–1.15	7.5–12.5	60	—	17.2	32.4	104
2	1	3.9–5.0	75	—	25	22.7	102
3	1	3.8–5.0	70	—	23.9	28	109
4	1	2.2–3.2	65	—	22.3	30.5	107
5	1	4.6–6.1	69	—	24.8	31	103
6	1.5	5.1	50	29.1	24.9	30.4	103.3
7	1.5	4.3	64.5	32.3	29.8	31.0	109.3
8	3.0	7.5–5.3	23	32.7	29.9	30.6	—
9	2	5.8	20	—	26.1	23.8	114.4
10	1.5	5.0	63.5	31.4	29.9	31.4	103.4
11	1.5	4.3	58	31.9	29.0	29.5	108.4
12	1	3.4	100	32.6	29.1	31.4	109.7
13	1	4.4	50	31.8	29.5	30.8	117

• The KBr concentration in the electrolyte was varied in the 5–10% range; the temperature was maintained between –32 and –34°; the O_2 feed rate was 100 cc/minute.

The active oxygen in the product reached 28–32%, and variations of current strength in the 1.5–3.0 amp range did not influence the active-oxygen content. It was found that at 3 amp (Experiment 8) the precipitate darkens and its structure deteriorates considerably.

There is every reason to believe that in large-scale experiments the amount of active oxygen in the product should be greater. In laboratory experiments, in the formation of relatively small amounts of the product, active oxygen could be lost as the result of traces of moisture entering the cell.

When the platinum cathode was replaced by molybdenum (Experiment 13), the active oxygen in KO_2 did not decrease; this shows that molybdenum may be used instead of platinum as cathode material.

Filtration and washing of the precipitate. The KO_2 precipitate was easily poured out of the cell through the bottom stopcock. The KO_2 precipitate was filtered and washed with the aid of glass filters and No. 20 glass fabric. Both these filter materials retain the precipitate almost completely, and may be recommended for use. The precipitate was washed with equal portions of ammonia (20–30 ml).

The precipitate was filtered and washed in the apparatus shown in Fig. 3. The glass vessel with a sealed-in glass filter A 35 mm in diameter, was kept in a Dewar vessel with liquid ammonia during the filtration. After each washing the KBr content of the precipitate and filtrate was determined; KBr in the filtrate was found from the weight of the residue after evaporation of ammonia.

The results obtained in removal of potassium bromide by washing are given in Table 2.

Fig. 3. Apparatus for filtration and washing of the KO_2 precipitate.

It is seen that the amount of potassium bromide in the precipitate can be decreased by thorough washing; repeated washing with relatively large amounts of solvent is necessary.

The product was analyzed for its mercury content. Qualitative tests (saturation with hydrogen sulfide of an acidified solution obtained after decomposition of 1-2 g of the substance) and spectroscopic analysis did not reveal any noticeable traces of mercury.

TABLE 2
Results of Experiments on Washing of KO₂ Precipitate*

Washing No.	KBr content (% on wt. of KO ₂)	KBr conc. in filtrate (%)	Notes
0	34	10	Weight of KO ₂ 3.96 g; 20 cm ³ of ammonia for each washing; temperature - 35°
I	16	3.5	
II	9.3	1.3	
III	7.1	0.5	
IV	6.0	0.2	
V	4.8	0.2	
VI	3.9	0.15	
0	34	10	Weight of KO ₂ 1.75 g; 30 cm ³ of ammonia for each washing; temperature - 35°
I	8.7	1.4	
II	5.7	0.2	
III	3.2	0.15	
IV	2.2	0.05	

* A. V. Ankudimov took part in the experiments detailed in Tables 1 and 2. These results were confirmed by experiments performed in the Karpov Institute (Professor V. A. Pleskov's laboratory).

The closed-cycle process was effected in the Plexiglas apparatus shown schematically in Fig. 4.

Aqueous KOH solution was electrolyzed in a cell with a mercury cathode (in laboratory experiments KOH was used instead of KC1, which simplified the apparatus). The potassium amalgam containing 0.1-0.2 % potassium, formed in the cell 1, was raised by means of the elevating device 2 through the system of seals 3 and 4 into the reactor 5. The amalgam was anodically oxidized in the reactor. The electrolyte was KBr solution in liquid ammonia. The cathode was the platinum spiral 6.

Oxygen passed through the drying tube 8 to the sprayers 7. The ammonia was dried over metallic sodium in the cylinder 9. Dry ammonia passed from the cylinder into the condenser 10, and was then poured into the reactor.

The KO₂ was deposited on the amalgam surface in the form of a microcrystalline mobile powder.

The accumulating precipitate passed to the filter 11; glass fabric was used as the filter material in the form of bags 12 fixed on a rubber bung. The vacuum in the filter was produced by means of the vacuum pump 13. The mother liquor was collected in the receiver 14, from which it was returned to the reactor.

Dry liquid ammonia was fed into the bag from a reservoir in order to wash the KO₂.

It has been reported [7] that explosions took place in contact of mercury with ammonia, owing to formation of dehydration products of Millon's base, formed directly or indirectly by combination of mercuric oxide with ammonia. Therefore, complete isolation of the alkali metal from the amalgam was avoided. The presence even of traces of alkali metal in the amalgam excludes the possible formation of mercuric oxide and subsequently of Millon's base.

Preliminary economic estimates show that the production cost per ton of KO₂ made by direct electrochemical synthesis should be considerably below existing costs.

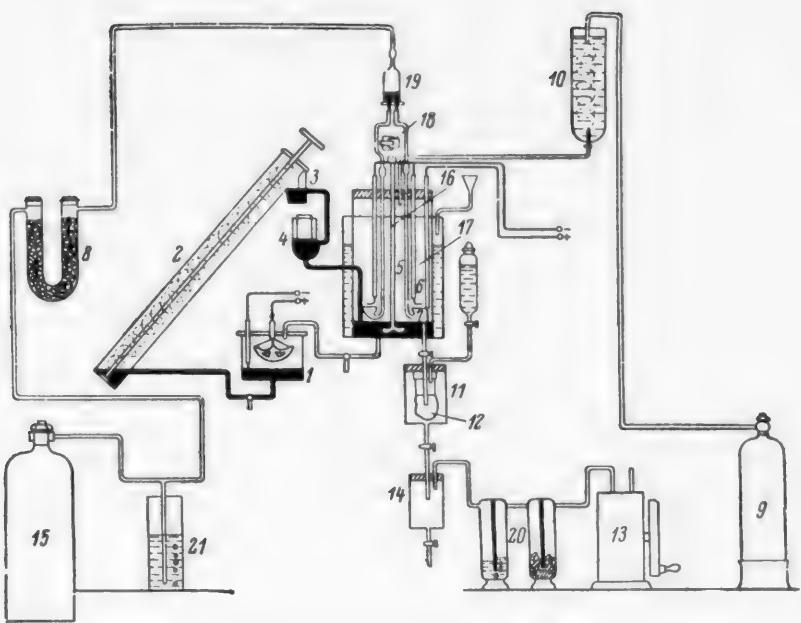


Fig. 4. Apparatus for electrochemical synthesis of KO_2 . 1) Cell; 2) mercury elevator; 3, 4) mercury seal; 5) reactor; 6) electrode; 7) sprayer; 8) drier; 9) NH_3 cylinder; 10) condenser for NH_3 ; 11) filter; 12) filter bag; 13) vacuum pump; 14) filtrate receiver; 15) O_2 cylinder; 16) stirrer; 17) electrode; 18) stirrer motor; 19) gas distributor; 20) Tishchenko flasks; 21) manostat.

SUMMARY

It is shown that KO_2 can be produced by direct electrochemical synthesis, by anodic oxidation of potassium amalgam in a solution of potassium bromide in liquid ammonia, with simultaneous oxidation of the solution of potassium in ammonia, formed at the cathode, by molecular oxygen; the process characteristics are: current density (anodic) 10 amp/ dm^2 , electricity consumption per kg KO_2 500 amp-hrs, power consumption per kg 5 kw-hrs, KO_2 production per m^2 anode area 2 kg/hr.

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MECHANISM OF INCOMPLETE OXIDATION OF METHANE IN PRESENCE OF NITROGEN OXIDES

S. F. Gudkov

One method for production of formaldehyde is incomplete oxidation of natural gas in presence of nitrogen oxides. The mechanism of methane oxidation has been studied by several workers [1-4]. It has now been established that it proceeds by a chain reaction. Many radical chain schemes have been proposed to account for its mechanism. For example, according to Norrish the oxidation chains in presence of nitrogen oxides are initiated by oxygen atoms formed as the result of oxidation of nitric oxide:



Lewis and von Elbe consider that the methane-oxidation chains are initiated at the surface:



A defect of these and a number of other schemes is that they are all hypothetical in character. The explanation is that because of the diversity of the conversion stages and the difficulty in identifying the active centers and radicals involved in the individual stages it is difficult to determine the true course of the process. There is very little experimental information on the subject, so that substantiated conclusions cannot be drawn.

Since the yield of formaldehyde in the oxidation of methane is considerably below the thermodynamically possible, determination of the mechanism of this reaction is of great theoretical as well as practical interest.

The present communication contains the results of a study of the role of nitrogen oxides in the incomplete oxidation of methane.

EXPERIMENTAL*

The usual flow unit was used for investigations of the oxidation reaction. The reactor was a quartz tube of 14 mm inside diameter, packed with broken porcelain. The tube was heated electrically. The heating zone was so chosen that the residence time of the gaseous mixture in the reaction space was 0.08 second.

Atmospheric oxygen was used for oxidation of methane. The methane:air ratio in all the experiments was 1:2. The feed rate of the methane-air mixture was 1200 ml/minute. Nitrogen oxides were fed directly into the reaction zone through a capillary tube 0.2 mm in diameter. The residence time of nitrogen oxides in the capillary tube did not exceed 0.005 second, so that reactions which might distort the results could not take place in the tube.

Natural gas containing 92-93% methane was used for the work. The gas was passed through a column packed with activated carbon to remove higher homologs of methane before entering the reactor. Nitrogen oxides were prepared by the reaction of sodium nitrite and ferrous sulfate in an acid medium. Before entering the reaction zone, the nitrogen oxides were freed from higher oxides of nitrogen and moisture by 30% alkali solution and calcium chloride. The NO and NO₂ concentrations were varied by oxidation of part of the NO to NO₂ by oxygen.

* L. I. Kryuchkova took part in the experimental work.

Nitrogen oxides were analyzed by a modification of the method developed by the State Institute of the Nitrogen Industry [6]. The NO and NO_2 contents were determined separately by means of sulfanilic acid and α -naphthylamine. Nitrogen dioxide gave a rose-red color with this reagent. The intensity of the color was compared with that of a standard solution prepared from sodium nitrite. The determination was performed by means of the FEK-M photoelectric colorimeter. After absorption of the nitrogen oxide, the nitric oxide remaining in the reaction gas was oxidized by potassium permanganate to give nitrogen dioxide again; this was determined by absorption in a solution of sulfanilic acid and α -naphthylamine. Nitrogen was blown through the entire system before and after absorption of the nitrogen oxides. The results were fairly concordant, and the experimental error did not exceed 5%.

RESULTS AND DISCUSSION

For elucidation of the role of nitrogen oxides in the incomplete oxidation of methane, study of the effects of temperature on the concentration of NO and NO_2 in the reaction gas is of the greatest importance. This relationship was studied in the 300-700° temperature range. Nitrogen oxides in an NO: NO_2 ratio of 3 were fed

into the reaction zone. The experimental results are plotted in Fig. 1. The amount of formaldehyde actually formed is a measure of the extent of the oxidation process. It was determined as the sum of the amount of formaldehyde found by analysis and the carbon monoxide and dioxide in the gas, formed in further conversion of formaldehyde.

A 1:2 methane-air mixture was used in the experiments of this series. For comparison, the behavior of nitrogen oxides in streams of air and methane respectively was studied under analogous conditions.

It is seen in Fig. 1 that both the concentration of nitrogen oxides and the ratio of the individual components (NO and NO_2) varies with the temperature.

The concentration of nitrogen oxides remains unchanged up to 580 to 600° (within the limits of analytical error), and decreases above this temperature.

Curves 2 and 3 show that the concentrations of the individual components (NO and NO_2) alter unequally.

The concentration of nitric oxide falls somewhat with increase of temperature. The explanation is that a part of it is converted into nitrogen dioxide in presence of air:



The concentration of nitrogen dioxide increases in the process. However, above 580-600° the concentration of NO_2 falls sharply. Thus, the change of the total concentration of nitrogen oxides is caused mainly by the change in the concentration of nitrogen dioxide.

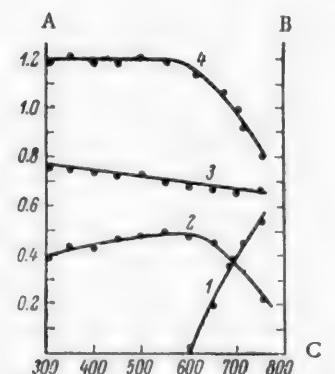


Fig. 1. Effect of temperature on the amount of formaldehyde actually formed and concentration of nitrogen oxides. A) Concentration of NO and NO_2 (ml/liter); B) amount of CH_2O actually formed (%); C) temperature (in °C).
1) Amount of formaldehyde actually formed, 2) NO_2 concentration in gas, 3) NO concentration in gas, 4) total content of nitrogen oxides.

The existence of a critical temperature which divides the curve for the nitrogen dioxide content into two branches with different slopes indicates that nitrogen dioxide enters a chemical reaction. In all probability the nitration of methane is such a reaction, under the given experimental conditions, involving consumption of nitrogen oxides. It is probably accompanied by side processes in which the nitro compounds formed are decomposed, so that part of the O_2 is in a mobile state and is exchanged between the nitrogen oxides in the gas phase and the nitro groups in the nitration products. Moreover, apart from the nitration process, nitrogen dioxide in all probability acts as an oxidizing agent, being reduced to nitric oxide, which is oxidized again to NO_2 by atmospheric oxygen.

It should be noted that the temperature at which the concentration of nitrogen oxides begins to decrease coincides with the temperature at which formation of oxygen-containing compounds — formaldehyde, carbon monoxide, and carbon dioxide — begins. Moreover, as examination of Curves 1 and 4 in Fig. 1 shows, the amount

of formaldehyde actually formed increases in proportion to the amount of nitrogen oxides lost. This effect indicates that the yield of oxygen-containing products is closely associated with chemical reactions involving nitrogen oxides. By reacting with stable molecules in two directions (nitration and oxidation) nitrogen oxides can form free radicals which initiate chain reactions of further hydrocarbon oxidation. A scheme for the initiation and growth of reaction chains in hydrocarbon nitration was put forward earlier [6].

The occurrence of this nitration reaction is also confirmed by experiments on the behavior of nitrogen oxides in separate air and methane streams, respectively. The experimental conditions were the same as in the case of the methane-air mixture. The concentration of nitrogen oxides in the initial mixture was 1.5 ml per liter of reaction gas in both cases.

Figure 2 shows the effect of temperature on the concentration of nitrogen oxides and the NO:NO₂ ratio in the case of air. The analogous relationships for methane are plotted in Fig. 3. The scale of the NO:NO₂ ratio (the right-hand ordinate axis) for the air stream is 5 times the scale for the methane stream.

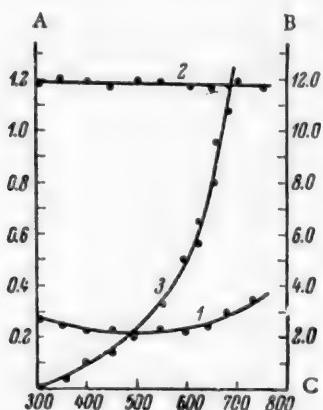


Fig. 2. Effect of temperature on the concentration of nitrogen oxides and the NO:NO₂ ratio in an air stream. A) Concentration of NO and NO₂ (ml/liter); B) NO:NO₂ ratio; C) temperature (in °C). 1) NO:NO₂ ratio, 2) total content of nitrogen oxides, 3) equilibrium NO:NO₂ ratio.

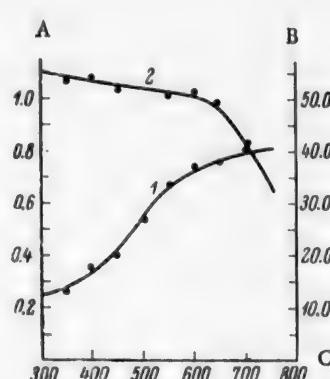


Fig. 3. Effect of temperature on the concentration of nitrogen oxides and the NO:NO₂ ratio in a methane stream. A) Concentration of NO and NO₂ (ml/liter); B) NO:NO₂ ratio; C) temperature (in °C). 1) NO:NO₂ ratio, 2) total content of nitrogen oxides.

Comparison of these graphs shows that whereas in the air stream the absolute concentration of nitrogen oxides remains almost unchanged with changes of temperature, in the methane stream the content of nitrogen oxides falls (slowly at first, and more rapidly starting at 580-600°).

The NO:NO₂ ratio is much higher in the methane than in the air stream. The NO:NO₂ ratio increases with the temperature in both cases, but this increase is much more rapid in the methane stream. At 500-800° the nitrogen oxides in the methane stream actually contain 96-97% NO. The explanation is that part of the NO₂ is expended for nitration of methane, and that no oxygen to oxidize NO to NO₂ is present in the mixture. On the other hand, the NO₂ content is high in the air stream. Curve 3 in Fig. 2 represents the equilibrium NO:NO₂ ratio calculated for the given experimental conditions. Comparison of Curves 1 and 3 shows that under these experimental conditions the NO:NO₂ ratio does not reach the equilibrium value, because of the short time (0.08 second) during which the gas mixture remains in the reaction space.

We studied variations of the NO:NO₂ ratio with the composition of the nitrogen oxides fed into the methane-air mixture. The contents of NO and NO₂ in the nitrous gases were varied by oxidation of a part of the NO by oxygen in an intermediate vessel of definite volume. Nitrogen oxides with NO:NO₂ ratios of 0.2, 0.3, 1.2, and 2.5 were fed into the methane-air mixture. The amount of nitrogen oxides in the original mixture was the same in

all the experiments of this series. Curves for the formaldehyde content of the reaction gas as a function of the temperature were plotted for each of these ratios. The temperature was varied from 300 to 800° in these experiments. The results are given in Fig. 4. Curves 1-4 represent variations of the NO : NO₂ ratio with the temperature, and Curves I-IV represent the formaldehyde concentrations in the reaction gas at the corresponding NO : NO₂ ratios. It is seen that the NO : NO₂ ratio varies with the temperature in such a manner that at 690-700° all the curves intersect at one point. At this temperature the NO : NO₂ ratio is approximately 2.9-3.0 in all cases, irrespective of the ratio in the original mixture; this shows that at this temperature equilibrium is established between NO, NO₂, and the other components of the reaction gas.

The formaldehyde concentration at 690-700° was almost the same in all cases, 0.86-0.90 volume percent. Below this temperature the relationship between the NO : NO₂ ratio and the formaldehyde concentration in the reaction gas is such that the lower the ratio, the higher is the formaldehyde yield. In other words, the higher the concentration of nitrogen dioxide, the greater is the yield of formaldehyde. If nitrogen oxides with a lower content of nitrogen dioxide are used, a higher temperature is required for the same yield of formaldehyde.

Study of the effects of temperature on the formaldehyde yield and the NO : NO₂ ratio leads to the conclusion that the reaction of incomplete oxidation of methane is accelerated by NO₂, and not by NO as was formerly believed [3].

This conclusion is also confirmed by experiments conducted with different amounts of nitrogen oxides fed into the methane-air mixture. The experimental results are given in Fig. 5. As before, 1-4 represent curves for variations of the NO : NO₂ ratio, and I-IV are curves for the formaldehyde concentration in the converted gas. Curve 1 represents variations of the NO : NO₂ ratio for a mixture containing 0.5 ml of nitrogen oxides per liter. Curves 2, 3, and 4 correspond to contents of 1.0, 2.0, and 4.0 ml of nitrogen oxides per liter.

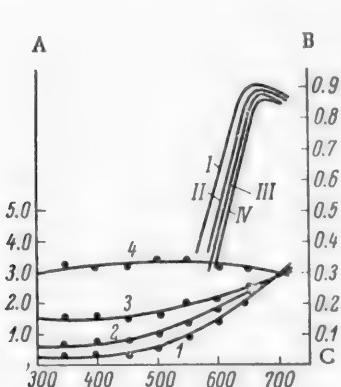


Fig. 4. Effect of temperature on the NO : NO₂ ratio and formaldehyde yield for a 1 : 2 methane-air mixture. A) NO : NO₂ ratio; B) amount of CH₂O formed (%); C) temperature (in °C). 1-4) NO : NO₂ ratio in the reaction gas at NO : NO₂ ratios in the original mixture of 2.10, 0.52, 0.44, and 0.30, respectively; I-IV) respective formaldehyde yields at the above NO : NO₂ ratios.

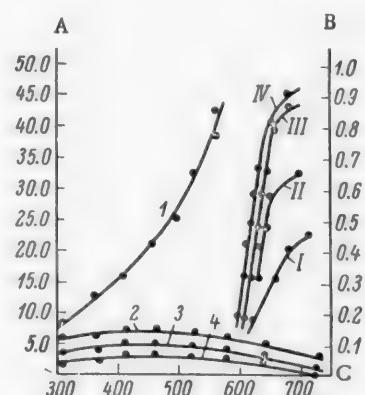


Fig. 5. Variations of NO : NO₂ ratio and formaldehyde yield in 1 : 2 methane-air mixture. A) NO : NO₂ ratio; B) amount of CH₂O formed (%); C) temperature (in °C). 1-4) NO : NO₂ ratio in the reaction gas with nitrogen oxide contents in the original mixture of 0.5, 1.0, 2.0, and 4.0, respectively; I-IV) respective formaldehyde yields at the above NO : NO₂ ratios.

It is clear from the graph that the formaldehyde concentration in the converted gas increases with increasing nitrogen oxide content in the original mixture. However, this increase continues only up to the maximum formaldehyde content, which is 0.90-0.95 volume percent in our experimental conditions.

The less nitrogen oxides is fed into the reaction mixture, the higher is the NO:NO₂ ratio. The probable explanation is that when the content of nitrogen dioxide in the reaction mixture is low it is lost more rapidly from the system because it is expended for nitration and oxidation of the hydrocarbon.

S U M M A R Y

During incomplete oxidation of methane in presence of nitrogen oxides the latter react chemically with stable methane molecules with formation of free radicals which initiate methane oxidation reaction chains. NO₂ acts as an accelerating agent in this reaction.

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CONVERSION OF METHANE INTO CARBON DISULFIDE BY MEANS OF SULFUR DIOXIDE

V. T. Vdovichenko, N. P. Galenko, and A. V. Larionov

Carbon disulfide is an important chemical in the industrial production of viscose rayon, carbon tetrachloride, and potassium thiocarbonates, and is used widely in many industries as a solvent for fats, oils, and resins. At the present time carbon disulfide is made industrially by the action of sulfur vapor on wood charcoal in fired or electrically-heated retorts at 900-1000° [1].

The production of carbon disulfide from natural gas (methane) and sulfur or its compounds—hydrogen sulfide, sulfur dioxide—which are by-products of many industries is a problem of scientific and technical interest.

Investigations [2-8] of methods for the production of carbon disulfide from sulfur vapor and methane, or from hydrogen sulfide and methane, have shown that conversion of methane into carbon disulfide in these processes is accompanied by absorption of heat, and requires temperatures of 800-1000°.

The literature on the reaction of sulfur dioxide with methane to give carbon disulfide is inadequate.

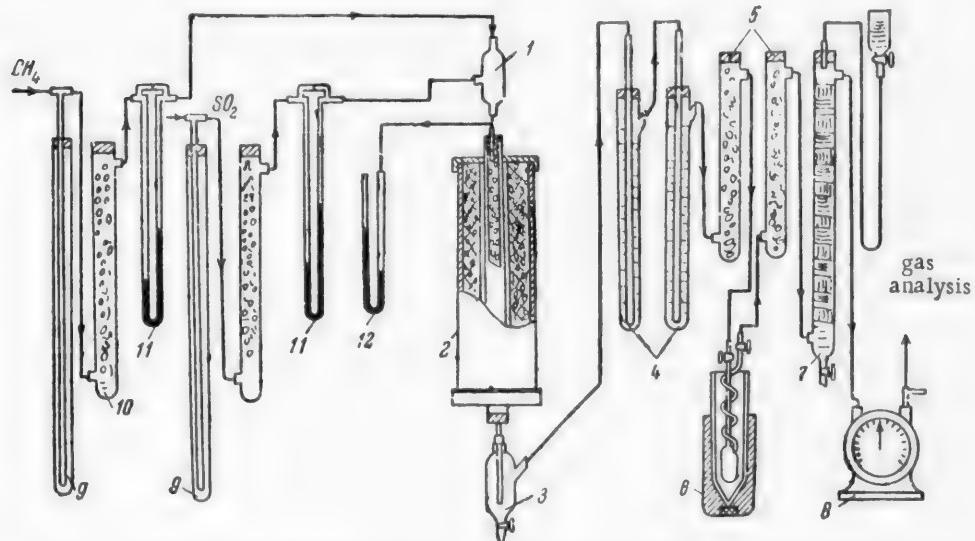


Fig. 1. Laboratory unit for conversion of methane into carbon disulfide by means of sulfur dioxide. 1) Mixer; 2) reaction tube; 3) trap for sulfur and water; 4) bubblers with a solution of I_2 in KI ; 5) $CaCl_2$ columns; 6) low-temperature trap for carbon disulfide; 7) scrubber; 8) gas meter; 9) regulator of methane and sulfur dioxide pressure; 10) $CaCl_2$ columns; 11) rheometers.

The purpose of the present work was to study the conditions of interaction of methane with sulfur dioxide for the production of carbon disulfide.

The experiments were performed in a flow system shown schematically in Fig. 1. Measured amounts of sulfur dioxide and natural gas containing 98 vol. % of methane were mixed in the mixer 1 and then passed into the porcelain tube 2 packed with catalyst. The reaction tube, 15 mm inside diameter and 600 mm long, was heated in an electric furnace.

The reaction products passed through the trap 3 to condense water and sulfur vapors and through the bubblers 4 to remove hydrogen sulfide and residual sulfur dioxide, and after being dried in the calcium chloride columns 5 they passed to the low-temperature trap 6 for condensation of carbon disulfide, the scrubber 7 to remove carbon dioxide, and the gas meter 8 for measurement of the amount of residual gas. The amounts of water, sulfur, and carbon disulfide in the reaction products were found by weighing of the traps. Hydrogen sulfide and unchanged sulfur dioxide were absorbed in a solution of iodine in potassium iodide, in which hydrogen sulfide was oxidized to sulfur and sulfur dioxide to SO_4^{2-} [9]. The amount of carbon dioxide absorbed by caustic soda solution in the scrubber 7 was determined by titration of equal samples of the liquid with hydrochloric acid solution [10]. The amounts of hydrogen, carbon monoxide, and unchanged methane in the reaction products were determined by means of the VTI gas-analysis apparatus in average gas samples taken at the exit from the gas meter.

TABLE 1
Yields of CS_2 and Distribution of Sulfur in the Reaction Products with Different Catalysts, at Space Velocities of CH_4 and SO_2 Between 360 and 380 hr^{-1} and CH_4/SO_2 Ratios Between 3 and 4

Catalysts	Yield of CS_2 per liter SO_2 (g)	Distribution of sulfur in reaction products (wt. %)			
		CS_2	S	H_2S	unchanged SO_2
Alumina gel	0.1	5.8	24.6	69.7	0.2
Bentonite clay	0.4	26.7	5.2	67.9	0.2
The same, impregnated with Pb^{++}	0.6	45.0	14.5	30.0	10.5
The same, impregnated with Fe^{++}	0.4	20.1	46.3	21.3	12.3
Pumice impregnated with Pb^{++}	0.8	47.1	1.9	18.8	32.2
Silica gel impregnated with Pb^{++}	0.1	15.3	2.5	80.5	1.7

TABLE 2
Variations of CS_2 Yield and Sulfur Distribution in the Reaction Products with Temperature at Space Velocity from 360 to 380 hr^{-1} and CH_4/SO_2 Ratio Between 3 and 4, With Pumice and Bentonite Impregnated with Pb^{++}

Characteristics	Pumice + 5% Pb^{++}				Bentonite + 5% Pb^{++}				
	700°	800°	900°	1000°	750°	800°	850°	900°	1000°
Yield of CS_2 per liter of SO_2 (g)	0.22	0.80	0.92	0.80	0.39	0.49	0.41	0.43	0.37
Sulfur distribution in reaction products (wt. %):									
CS_2	20.0	49.4	60.0	47.1	23.0	30.4	21.4	25.2	22.2
S	1.3	2.9	0.5	1.9	6.1	0.5	11.9	5.4	6.1
H_2S	70.7	28.8	20.3	18.8	70.0	68.5	65.7	69.1	70.5
Unchanged SO_2	8.0	19.2	19.2	32.2	0.9	0.6	1.0	0.3	1.2

The catalysts tested were alumina gel and Oglanli bentonite clay in the pure state; and also pumice, "KSK" silica gel, and Oglanli bentonite impregnated with the salts



and then heated. The metal ion contents of the catalysts were 5% of the weight of support.

The average experimental results are presented in Tables 1-3 and Fig. 2.

TABLE 3
Variations of CS_2 Yield and Sulfur Distribution
in the Reaction Products, Formed over Pumice
Impregnated with Lead Acetate, with the
 CH_4/SO_2 Ratio at Space Velocity 570-600
 hr^{-1} and Temperature 900°

CH_4/SO_2	Yield of CS_2 per liter SO_2 (g)	S distribution in reaction products (wt. %)			
		CS_2	S	H_2S	un- changed SO_2
0.53	0.30	19.5	6.9	25.3	48.3
1.25	0.65	37.4	13.1	27.2	22.3
1.26	0.67	39.7	28.7	27.0	4.6
3.10	0.92	60.0	0.5	17.3	19.2

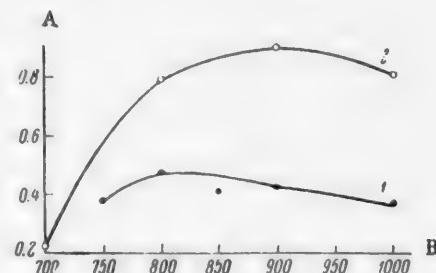


Fig. 2. Effect of temperature on the CS_2 yield. A) Yield of CS_2 per liter SO_2 (g); B) temperature (in °C); 1) bentonite clay, 2) pumice impregnated with $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ solution.

It is clear from Table 1 that pumice treated with lead acetate is the most active catalyst as indicated by the weight yield of carbon disulfide per unit volume of sulfur dioxide fed into the reaction mixture.

Figure 2 and Table 2 show that the optimum temperatures for formation of carbon disulfide on pumice and bentonite impregnated with lead acetate are 900 and 800°, respectively.

With increase of the $\text{CH}_4:\text{SO}_2$ ratio from 0.5 to 3 (Table 3) the carbon disulfide yield increases from 0.3 to 1 g liter of SO_2 .

In all the experiments the gaseous reaction products at the exit from the gas meter contained from 5 to 12% carbon dioxide, 2 to 8% carbon monoxide, 5 to 20% hydrogen, 0.5 to 1% unsaturated compounds, 0.6 to 3% carbonyl sulfide (all volume percentages), and also some unchanged methane. The CO_2 , CO , H_2 , and COS contents of the gas increase with the process temperature. Fractional distillation of the carbon disulfide yielded 98% of a fraction boiling in the 45-47° range.

SUMMARY

- Investigations of the conversion of methane by means of sulfur dioxide over various catalysts and under different experimental conditions have shown that carbon disulfide may be produced by this process.
- The best of the catalysts tested for the production of carbon disulfide from methane and sulfur dioxide (0.8 g per liter of sulfur dioxide) is pumice impregnated with lead acetate.
- Change of the $\text{CH}_4:\text{SO}_2$ ratio from 0.5 to 3, under the experimental conditions used, increases the CS_2 yield from 0.3 to 1 g per liter of SO_2 used.

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CONCENTRATION OF SODIUM HUMATE SOLUTIONS

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The production of alkaline humates in the form of concentrated solutions is a problem of immediate importance. If the problem could be solved, it would be possible to organize production of these reagents directly at the sources of brown coal, with a lowering of material costs and labor requirements in the production of clay suspensions at the drilling sites.

Aqueous solutions of sodium humates, made by the action of caustic soda on brown-coal suspensions, are mainly used for stabilization of the clay suspensions used in oil-well drilling. Alkali humate solutions are usually prepared at the drilling site, which is very disadvantageous economically for the following reasons.

The amount of humic acids extracted from the coal in the production of alkaline humate solutions does not exceed 10-15%, while the rest of the coal is a waste product which is rarely used for any purpose. Thus, a large proportion of the transport costs corresponds to a component of the coal which is (in this case) useless.

Aqueous humate solutions are made at the drilling sites by a very primitive process, and this also raises costs.

It is quite evident that production of sodium humate solutions by a factory process is much more economic, but only if they are obtained in concentrated form, as transport of dilute humate solutions to the drilling sites can hardly be economically efficient.

Alkaline humate suspensions can, in principle, be concentrated by two methods: by removal of excess water by evaporation, and chemically, by precipitation of humates by means of a suitable reagent with subsequent mechanical separation of the liquid phase from the precipitate. Despite its simplicity, evaporation is economic only if cheap sources of heat (such as waste-gas heat, etc.) are used to heat the solutions. Generally, cheaper methods of concentration are sought; of these, chemical methods are the most attractive.

It was shown in our earlier investigations [1] and in studies by other authors [2] that alkali humate solutions are coagulated by addition of sodium chloride. This fact is very important if the precipitates formed by the coagulation method are spontaneously peptized by addition of water without preliminary washing. In that case, coagulative precipitation could form the basis of a method for the production of concentrated alkali humate solutions.

The use of sodium chloride as coagulant is very promising because of its availability, low costs, and the possibility of using mother liquors for preliminary treatment of the brown coal before extraction of humates by alkali solution [1].

EXPERIMENTAL

Sodium humate solutions were prepared as follows. To an aqueous suspension of finely-divided brown coal (from Aleksandriya, containing up to 35% humic acids and approximately 12% ash) a solution of caustic soda of known concentration was added, and the mixture was heated at 80-90° for 1-1.5 hours. The suspension was cooled, centrifuged to separate the solid residual brown coal from the solution, and the humate content in the solution was determined colorimetrically and gravimetrically.

Two samples of brown coal—native and extracted—were used for preparation of the humate solutions. The extracted coal differed from the native in containing no waxes, which had been extracted by means of hydrocarbons. Humate solutions obtained from extracted coal are more highly concentrated than those obtained from native coal under the same conditions. For example, treatment with 15% caustic soda solution gives a suspension containing 6.2% sodium humates in the case of native coal, and 8.2% in the case of extracted coal.

The use of extracted coal for production of suspensions is of considerable interest for the following reasons. In Aleksandriya (Ukrainian SSR) a factory has been built where wax is extracted (about 10% by weight) from brown coal. The extracted and dried coal is at present used for the same purposes as native coal.

If the production of concentrated alkali humate solutions could be organized at the extraction factory, there would be a considerable economic advantage, as costs of drying and transportation of the treated coal would be eliminated, the degree of humate extraction would be increased, etc.

A total of 6 solutions of sodium humates was prepared: from native coal in concentrations of 6.2% (No. 1) and 1% (No. 5), and from extracted coal in concentrations of 8.2% (No. 4), 3.2% (No. 2), and 1% (Nos. 3 and 6).

Coagulation of Sodium Humates in Alkali Humate Solutions of Different Concentrations By Addition of Saturated Salt Solution

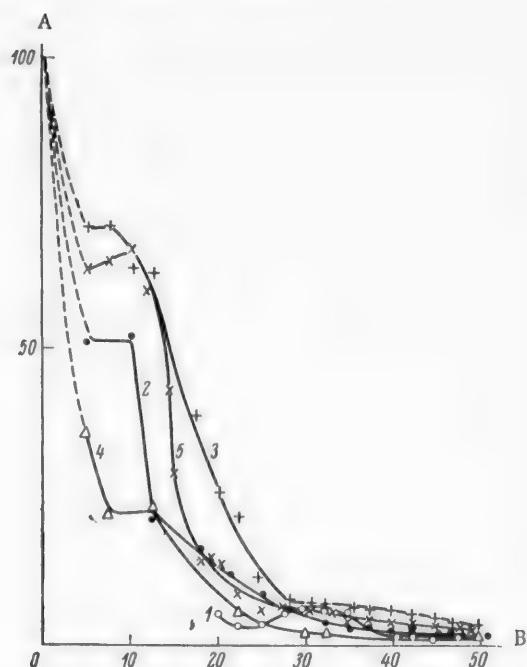
Amt. of humate solution (ml) <i>V₁</i>	Amt. of saturated NaCl solution (ml) <i>V₂</i>	<i>v₁/v₂</i>	Humate content in liquid phase after separation of precipitate (%)					
			from native coal		solutions from extracted coal			
			No. 5	No. 1	No. 6	No. 3	No. 2	No. 4
100.0	0	—	100	100	100	100	100	100
95.0	5.0	19.00	63.5	Gel	74.8	70.3	51.3	35.7
92.5	7.5	12.33	65.3	“	62.7	71.8	—	22.0
90.0	10.0	9.00	67.5	“	57.8	61.6	52.1	—
87.5	12.5	7.00	61.6	“	46.7	63.4	21.6	23.3
85.0	15.0	5.67	29.4	“	32.7	43.4	—	—
82.5	17.5	4.72	12.2	“	22.1	39.0	15.9	—
80.0	20.0	4.00	15.6	5.2	19.6	26.0	13.5	—
77.5	22.5	3.45	12.9	3.1	17.4	24.9	8.9	5.3
75.0	25.0	3.00	6.3	3.3	16.3	11.5	8.8	—
72.5	27.5	2.64	6.5	5.2	13.1	6.9	—	—
70.0	30.0	2.33	6.3	6.1	7.1	6.7	—	2.2
67.5	32.5	2.08	5.8	5.8	7.7	6.9	3.7	2.1
65.0	35.0	1.86	4.5	6.0	5.1	5.9	2.9	—
62.5	37.5	1.67	4.5	2.6	7.0	5.2	2.5	—
60.0	40.0	1.50	4.4	1.8	4.5	5.6	—	2.2
57.5	42.5	1.35	3.3	1.9	3.5	5.0	3.0	—
55.0	45.0	1.22	3.5	1.5	4.0	4.6	2.0	—
52.5	47.5	1.10	2.7	1.5	3.2	3.9	2.0	2.2
50.0	50.0	1.00	2.5	—	2.5	3.4	1.9	2.0

Saturated sodium chloride solution was used for coagulation. The total volume of humate and salt solutions was the same (100 ml) in each case, but their ratio was varied from 19:1 to 1:1. The precipitated sodium humates were separated from the salt solution in a centrifuge 48 hours after the mixing, and the residual sodium humates in the solution were determined. The humate concentration in a given solution before addition of the salt solution was taken as 100%. In the concentration determinations a correction was introduced for dilution of the original solution by the saturated sodium chloride solution. The dark solutions were diluted in a definite ratio to a color intensity convenient for colorimetric determination.

The results of the experiments are given in the table and the diagram.

DISCUSSION OF RESULTS

It follows from the experimental data that addition of a saturated solution of common salt to humate solutions at the concentrations studied causes coagulation in all cases. The amount of sodium humates remaining in the solutions decreases sharply with increase of the volume of salt solution added from 5 to 25%, and then remains almost constant. Comparison of the curves for different concentrations of the original solutions indicates that humates are isolated more completely from solutions of higher concentrations; this is very important from the practical standpoint.



Variation of sodium humate concentration in the liquid phase with the concentration of NaCl solution. A) Sodium humate content (%); B) concentration of NaCl solution (%). Concentration of sodium humate solutions (%): 1) 8.2; 2) 3.2; 3) 1.0; 4) 6.2; 5) 1.0. 1,2,3) Solutions from extracted coal; 4,5) solutions from native coal.

Saturated salt solution is added to the sodium humate solution in the coagulators (1 volume of NaCl solution to 4 volumes of humate solution), the liquid is heated by means of a steam jacket, cooled, and the solution of sodium chloride is separated from the alkali humate concentrate in a hydrocyclone. The reagent paste is packed in iron drums, while the salt solution is used for preliminary treatment of the brown coal in extractors.

Apart from its simplicity, the proposed process gives a higher utilization of coal and sodium chloride. If the production of alkali humate concentrates is organized in conjunction with utilization of the wastes from the extraction plant, even better economic characteristics can be attained.

SUMMARY

1. Coagulation of alkali humate solutions of different concentrations in relation to the amount of saturated sodium chloride solution added was studied; it was found that the amount of humates coagulated reaches a maximum (93-98%) when the volume ratio of the alkali humate solution to the saturated salt solution is about 2:1.

With more concentrated alkali humate solutions (6-8%) this ratio reaches 4:1, i.e., the humates are almost completely precipitated on addition of 1 volume of saturated salt solution to 4 volumes of alkali humate solution.

2. The precipitated sodium humates made by the coagulation method can be spontaneously peptized in water to give solutions with the properties of the usual alkali humate solutions.

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STUDY OF THE NITRATION OF BENZENE TO 2,4-DINITROPHENOL

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The term oxidative nitration is usually applied to the conversion of aromatic compounds directly into nitrophenols by the action of a mixture of mercuric nitrate and nitric acid of moderate concentration. Since the discovery of this reaction by Wolffenstein and Boeters [1] in 1906, many workers have studied the conversion of benzene into 2,4-dinitrophenol.

Several hypotheses were advanced in the earlier papers concerning the mechanism of this reaction. Some publications [2, 3] contained the hypothesis, later confirmed experimentally, that the arylmercury nitrate is formed at the first reaction stage, but the course of its further conversion into nitrophenols was not known.

Relatively recently, Titov and Laptev [4] have established the course of the reaction experimentally. They found that at the second reaction stage the arylmercury nitrate is converted into a nitroso compound, and that the formation of aryl diazonium nitrate is a side reaction, and not the principal direction as was formerly believed [2]. Other workers [5] reached similar conclusions.

The papers by Zakharov [6] and Bachmann [7], and certain patents [8, 9], are worthy of attention from the preparative and technical aspects.

Zakharov, who studied the oxidative nitration of benzene at moderate temperatures (from room temperature to 40°) with nitric acid and benzene in 5:1 molar ratio, found that the yield of 2,4-dinitrophenol increased with repeated use of the used oxidative-nitration mixture. In his technical experiments, performed at 35-40° with 59-60% nitric acid and 30% of mercury catalyst on the weight of benzene, the yield of dinitrophenol rose from 40% with the use of fresh nitration mixture to 80% when the used solutions were used for the fifth time. Picric acid and nitrobenzene were formed in very small amounts.

The optimum conditions determined by Bachmann are characterized by a higher molar ratio of nitric acid to benzene, a somewhat higher reaction temperature (50°), gradual addition of benzene, and a larger amount of mercury catalyst. The nitration mixture in his experiments was 10.65 molar with respect to nitric acid and 0.37 molar with respect to mercuric nitrate, while the nitric acid-benzene ratio was 13.3:1. The yield of 2,4-dinitrophenol was 68.4%, of picric acid, 4%, and of nitrobenzene, 7.8%.

These papers do not deal with the distribution of mercury at the end of the process and contain no data on the contamination of 2,4-dinitrophenol by mercury, while Zakharov did not even give the melting point of the dinitrophenol obtained in the description of his technical experiments.

It was of interest to study the course and results of oxidative nitration of benzene to dinitrophenol at the two molar ratios of nitric acid and benzene indicated above, with the same composition of the oxidative-nitration mixture and at the same temperature, and to determine the distribution of mercury at the end of the experiments.

Our experiments were performed at 17-22° with a nitration mixture close in composition to that used by Bachmann. Fresh nitration mixture was used only in the first experiments, while in the subsequent experiments filtrates from the previous experiments were used after the nitric acid concentration had been restored to the initial level.

The results of the experiments are given in Table 1, and the mercury distribution in Table 2. It follows from Table 1 that the total yield of 2,4-dinitrophenol was 71.1-75.1% in experiments in which the molar ratio of nitric acid to benzene was 13:1, and only somewhat above 53.5% in experiments with 5:1 ratio.

TABLE 1
Results of Experiments on Benzene Nitration

Expt. No.	Oxidative-nitration mixture	Amount of benzene (g)	Molar ratio of mercuric nitrate to benzene	Yield of 2,4-dinitro- phenol (%).		Mercury content of dinitrophenol (%)
				in pre- cipitate	in filtrate and wash liquors	
1	Freshly prepared	26.5	0.40	66.8	4.9	0.027
2	Filtrate from Expt. No. 1	17.0	0.38	68.7	6.4	0.030
3	Filtrate from Expt. No. 2	10.0	0.34	62.3	8.8	0.041
4	Freshly prepared	46.9	0.15	48.0	2.5	0.014
5	Filtrate from Expt. No. 4	28.1	0.15	53.5	Not determined	2.613

* The yields of dinitrophenol and picric acid are calculated on the benzene taken. The lower yield of dinitrophenol in Experiment 3 is attributable to incomplete conversion of benzene because of the lower temperature and lower mercury content in the nitration mixture.

TABLE 2
Mercury Distribution After Completion of Experiments

Expt. No.	Mercury found (% of amount taken)			total
	in 2,4-dinitro- phenol	in filtrate	in wash liquors	
1	0.04	96.77	3.18	99.99
2	0.05	92.36	4.79	97.20
3	0.07	94.95	2.48	97.50
4	0.04	97.21*	Not determined	—
5	8.64	84.45**	6.10**	99.19

* Including 4.81% as mercuric oxalate.

** Including mercury as oxalate.

In most cases the quality of the dinitrophenol as indicated by the melting point was good, with one exception (Experiment No. 5). Picric acid was found in the dinitrophenol in Experiment No. 5 only. Nitrobenzene was not determined quantitatively.

In the experiments with the reagents in 5:1 ratio, the filtrate from the dinitrophenol was found to contain considerable amounts of an insoluble mercury compound, which was precipitated when the filtrate was used as the nitration mixture in the following experiment and contaminated the dinitrophenol to a mercury content of 2.61% as compared with 0.014% in the preceding experiment. In experiments with 13:1 ratio the mercury content of the dinitrophenol rose from 0.027 to only 0.041% even after 3-fold use of the nitration mixture.

Since the literature reports of the formation of mercuric oxalate [2, 10] and basic mercuric nitrate [9] during oxidative nitration of benzene are not accompanied by analytical data, we analyzed the isolated mercury compound and identified it as mercuric oxalate.

In the above-mentioned paper by Bachmann the isolation of 2,4,2',4'-tetrannitrodiphenylamine (0.05% of the theoretical yield) in the oxidative nitration of benzene is reported. We isolated this compound from a mixture with 2,4-dinitrophenol in the oxidative nitration of benzene at 17-22° with a 5:1 ratio of nitric acid to benzene.

In work on a method for determination of picric acid in 2,4-dinitrophenol by precipitation with acridine, a molecular compound of 2,4-dinitrophenol and acridine of the composition $C_6H_4O_5N_2 + C_{13}H_9N$ was obtained.

EXPERIMENTAL

The experiments were performed in a two-necked flask with a reflux condenser and thermometer. The condenser was connected by an outlet tube to a system of Tishchenko flasks filled with nitrobenzene, concentrated sulfuric acid, and 40% caustic potash.

The benzene, nitric acid, and mercuric nitrate used in the experiments were chemically pure.

In Experiments Nos. 1-3, the molar ratio of nitric acid to benzene was 13:1, and in Experiments Nos. 4 and 5 it was 5:1; fresh nitration mixture was used in the first experiments only, and in the subsequent experiments filtrates from the previous experiments were used after the nitric acid concentration had been brought up to the initial level by addition of chemically pure 96% nitric acid. Fresh mercuric nitrate was added only after Experiment No. 4, as in this case its content decreased considerably owing to precipitation of mercuric oxalate. In the other experiments the decrease of the mercury concentration was relatively small.

The flask was charged with benzene and nitration mixture containing 50.5-51% of nitric acid and 4.9-4.7% (in Experiment No. 3, 4.2%) of mercuric nitrate calculated as mercury. In Experiments Nos. 1 and 4, performed with fresh nitration mixture, 0.05 g of sodium nitrite was also added in order to eliminate the induction period.

The reaction mixture was shaken thoroughly and left to stand at 17-22°, for 192 hours in Experiments Nos. 1-3, and for 550 hours in Experiments Nos. 4 and 5. The duration of the experiments was determined by the time required for the benzene taken to react. The mixture was shaken 4-5 times daily at 2-hour intervals. Experiments with different molar ratios of the reagents were performed in parallel.

The precipitated 2,4-dinitrophenol was filtered off and washed twice with 50% nitric acid and then 3 times with water. In each washing, 10 ml of 50% nitric acid or water per 10 g of benzene used in the experiment was taken. The precipitate was dried, and its melting point and mercury and picric acid contents were determined.

One third of the filtrate and one third of the wash liquors were extracted with benzene. The benzene extracts were treated with 30% triethanolamine in a separating funnel [7]. The remaining $\frac{2}{3}$ of the filtrate was used as the nitrating mixture in the next experiment, after addition of strong nitric acid.

The triethanolamine extract was acidified with concentrated hydrochloric acid to isolate a mixture of nitrophenols in which picric acid was determined with the aid of nitron [7], and 2,4-dinitrophenol by difference and by bromination with bromide-bromate, by a somewhat modified method [11]. The dinitrophenol content found by bromination corresponded to the difference between the weight of the mixture and the picric acid content found with the aid of nitron. Nitron picrate consisted of lemon-yellow fine crystals (from water), m. p. about 255° (decomp.); 257-258° by [12].

Found %: N 17.26, 17.47. $C_{28}H_{19}O_7N_7$. Calculated %: N 18.11.

Picric acid was determined in the dinitrophenol precipitate by means of acridine in ether solution at high dilution. Picric acid was found in a small amount only in nitrophenol from Experiment No. 5.

Nitrobenzene was not determined quantitatively, and its presence was detected from the odor of the nitrophenol and the benzene extracts.

The results of the experiments are given in Table 1.

The contents of nitric acid and mercury in the original and used nitration mixtures and the mercury contents of the wash liquors and dinitrophenol were determined by the method described in the literature [10].

The nitric acid concentration in the filtrates was 44.8-45.9% in Experiments Nos. 1-3, and 38.9-40.2% in Experiments Nos. 4 and 5.

Data on the contamination of dinitrophenol by mercury are given in Table 1, and the distribution of mercury after the end of each experiment is given in Table 2.

Mercuric oxalate. The pale yellow precipitate deposited in filtrate from Experiment No. 4 on standing was filtered off and washed with water, alcohol, and ether. Its weight was 1.32 g. The substance was insoluble in water and organic solvents, and soluble in nitric and (better) in hydrochloric acid; it gave qualitative reactions for Hg^{++} and $C_2O_4^{--}$ ions.

Found %: C 8.23, 8.26; H 0.23, 0.23; Hg 66.62, 66.04; $C_2O_4^{--}$ 29.7, 29.2. HgC_2O_4 . Calculated %: C 8.32; Hg 69.5; $C_2O_4^{--}$ 30.5.

The $C_2O_4^{--}$ ion content was determined by titration of a sample of the substance dissolved in dilute sulfuric acid with 0.1 N $KMnO_4$ solution.

From the filtrate of Experiment No. 5, 0.60 g of mercuric oxalate was isolated (most of it was precipitated before filtration and contaminated the 2,4-dinitrophenol). Small amounts of mercuric oxalate were also found in filtrates of Experiments Nos. 2 and 3, performed at 13:1 ratio of nitric acid to benzene.

2,4,2',4'-tetranitrodiphenylamine. The wash liquor of Experiment No. 4 contained a small quantity of a dark brown oily liquid which crystallized after prolonged standing. This gave 0.3 g of an orange precipitate consisting of a mixture of 2,4-dinitrophenol with tetranitrodiphenylamine. The mixture was separated by treatment with ether. The undissolved portion (0.02 g, m. p. 195.5-200°) was recrystallized from alcohol. It gave yellow crystals, m. p. 200.9-202.1°. According to literature data, 2,4,2',4'-tetranitrodiphenylamine has m. p. 201-201.5° [13].

The substance dissolves with difficulty in the usual solvents, and has very weak acidic properties. The action of caustic soda or ammonia on its solutions in alcohol or ether results in an intense red color.

Found %: N 20.46. $C_{12}H_7N_5O_8$. Calculated %: N 20.06.

The dark red ether solution was washed with caustic soda to extract 0.15 g of substance with m. p. 111.8 to 112.7°, which did not give a melting point depression when mixed with pure 2,4-dinitrophenol. The ether layer, after being washed with water and dried, yielded a further 0.02 g of contaminated tetranitrodiphenylamine.

The molecular compound of 2,4-dinitrophenol with acridine was prepared by mixing of solutions of 0.2 g of 2,4-dinitrophenol in 5 ml of alcohol and 0.23 g of acridine in 5 ml of ether. The precipitate was filtered and washed with ether; yield 0.12 g. Yellow needles (from water), m. p. 162.5-163°.

The compound dissolves with difficulty in the cold in acetone, alcohol, and benzene, and with greater difficulty in ether and water.

Found %: $C_6H_5(NO_2)_2OH$ 51.10, 50.88; C 62.52, 62.50; H 4.00, 3.97; N 11.50, 11.54. $C_{19}H_{13}O_5N_3$. Calculated %: $C_6H_5(NO_2)_2OH$ 50.67; C 62.81; H 3.61; N 11.57.

The percentage content of dinitrophenol was determined by titration of an alcoholic solution of the compound by caustic soda in presence of phenolphthalein.

SUMMARY

1. Comparative experiments on the oxidative nitration of benzene at moderate temperatures, with 5:1 and 13:1 ratios of nitric acid to benzene, showed that the yield of 2,4-dinitrophenol increases with increasing amount of nitric acid.

2. The distribution of mercury at the end of the experiment, and the contamination of 2,4-dinitrophenol by mercury, were determined. It was found that at the lower nitric acid—benzene ratio repeated use of previously used nitration mixture results in considerable contamination of the dinitrophenol with a mercury compound, identified as mercuric oxalate. Formation of the latter leads to a decrease in the concentration of the mercury catalyst in the acid solution.

3. The reported formation of 2,4,2',4'-tetranitrodiphenylamine in the oxidative nitration of benzene [7] was confirmed.

4. A molecular compound of 2,4-dinitrophenol with acridine, having the composition $C_8H_4O_5N_2 + C_{13}H_9N$ was prepared.

The author offers his gratitude to S. V. Bogdanov for his help in the course of this investigation.

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EFFECTS OF THE TETRAALKYL DIAMIDES AND DIPIPERIDIDES OF
UNSATURATED PHOSPHONIC ACIDS ON THE ANTIOXIDANT
PROPERTIES OF MINERAL OIL

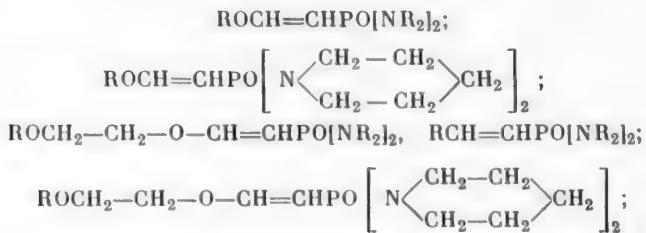
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The influence of fully esterified unsaturated phosphonic acids on the antioxidant properties of MS-20 oil was described in the previous paper [1].

The present paper contains the results of a study of the influence of diamides and dipiperidides of unsaturated phosphonic acids on the antioxidant properties of the same oil.

Compounds of the following types were prepared for the investigation:



where R—CH₃, C₂H₅, C₃H₇, C₄H₉, C₆H₅.

All the tetraalkyl diamides and dipiperidides of β -alkoxy(phenoxy) vinylphosphonic, β -ethoxyethoxyvinylphosphonic, and phenylvinylphosphonic acids were prepared by the action of the corresponding acid dichlorides on dialkyl amines or piperidine in ligroine [2].

The tetrabutyldiamide of β -ethoxyethoxyvinylphosphonic and the dipiperide of β -butoxyvinylphosphonic acid (AP-21, AP-35) were prepared as indicated above.

The tetraethylamides and dipiperidides of β -alkoxy(phenoxy) vinyl phosphonic, β -ethoxyethoxyvinylphosphonic, and phenylvinylphosphonic acids are liquids or solids which dissolve readily in the common organic solvents and mineral oils. All the substances are stable on keeping. The constants of the substances (boiling point, refractive index, and density) are given in Tables 1, 2, and 3.

The effects of these compounds on the antioxidant properties of MS-20 as indicated by the thermooxidative stability (T), volatility (E), working fraction (WF), and lacquer deposition (L), are given in the same tables.

For studies of the influence of the structure of the compounds on the antioxidant properties of the oil, the data in the tables are arranged according to the following system.

The right-hand side of the formula of each compound contains similar amide or dipiperide radicals: tetraethylamide in Table 1, tetrabutyldiamide in Table 2, and dipiperide in Table 3, while the left-hand side contains different unsaturated organic radicals: alkoxy(phenoxy) vinyl, phenylvinyl.

TABLE 1
Effect of Tetraethylamides of Unsaturated Phosphonic Acids on the Antioxidant Properties of MS-20 Oil

Code mark	Formula	Name of compound	Boiling point (in °C)	n_D^{20}	d_4^{20}	Engine prop. of MS-20 comp. 5731-53 (%)			Thermo-oxidative stability at 250° by the Papok method (min)
						E	WF	L	
MS -20	—	Oil	—	—	—	61	19	20	23
AP -58	$C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetraethylamide of β -ethoxyvinylphosphonic acid	126.5 (2 mm)	1.4755	1.0950	57	38	5	48
AP -59	$C_2H_9-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetraethylamide of β -butoxyvinylphosphonic acid	130 (2 mm)	1.4729	0.9745	55	40	5	46
AP -19	$C_2H_5-O-CH_2-CH_2-O-CH=CHPC[N(C_2H_5)_2]_2$	Tetraethylamide of β -ethoxyethoxyvinylphosphonic acid	146 (1 mm)	1.4749	1.0108	58	41	1	84
AP -22	$C_6H_5-CH=CH=CHPO[N(C_2H_5)_2]_2$	Tetraethylamide of β -phenylenvinylphosphonic acid	M. p. 103.5	—	—	47	53	0	88

TABLE 2
Effect of Tetrabutyldiamides of Unsaturated Phosphonic Acids on the Antioxidant Properties of MS-20 Oil

Code mark	Formula	Name of compound	Boiling point (in °C)	n_D^{20}	d_4^{20}	Engine prop. of MS-20 oil + 2% of compound, %			Thermo-oxidative stability at 250° by the Papok method (min)
						E	WF	L	
MS-20	$C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$	Oil Tetrabutyldiamide of β -ethoxyvinylphosphonic acid	172 (2 mm)	—	1.4680	0.9399	61	19	20
AP-28	$C_2H_5-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetrabutyldiamide of β -n-propoxyvinylphosphonic acid	172 (2 mm)	—	1.4678	0.9301	45	55	0
AP-29	$(CH_3)_2-CH-(CH_2)_2-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetrabutyldiamide of β -isooamyl oxyvinylphosphonic acid	192-193 (2 mm)	—	1.4691	0.9249	43	57	0
AP-32	$(CH_3)_2-CH-(CH_2)_2-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetrabutyldiamide of β -ethoxyethoxyvinylphosphonic acid	180 (1 mm)	—	1.4705	0.9579	48	52	0
AP-21	$C_2H_5-O-CH_2-CH_2-O-CH=CHPO[N(C_2H_5)_2]_2$	Tetrabutyldiamide of β -ethoxyethoxyvinylphosphonic acid	212 (0.5 mm)	—	1.5060	0.9886	47	53	0
AP-30	$C_2H_5-O-CH=CHPO[N(C_2H_5-H)_2]_2$	Tetrabutyldiamide of β -phenoxylphosphonic acid	M. p. 39-40	—	—	—	50	50	63
AP-31	$C_2H_5-O-CH=CHPO[N(C_2H_5-H)_2]_2$	Tetrabutyldiamide of β -phenylvinylphosphonic acid							

TABLE 3
Effect of Dipiperidinediamides of Unsaturated Phosphinic Acids on the Antioxidant Properties of MS-20 Oil

Code mark	Formula	Name of compound	Boiling point (in °C)	n_D^{20}	d_4^{20}	Engine prop. of MS-20 oil at 573° ^a : 53% ^b			Thermooxidative stability at 250° by the Papok method (min)
						E	WF	L	
MS-20 AP-34	$C_2H_5-O-CH=CHPO(NC_5H_{10})_2$	Oil Dipiperide of β -ethoxyvinyl- phosphonic acid	M. p. — 60—61	—	—	61 44	19 56	20 0	23 92
AP-35	$n-C_4H_9-O-CH=CHPO(NC_5H_{10})_2$	Dipiperide of β -butoxyvinyl- phosphonic acid	M. p. 37.5	—	—	44	56	0	103
AP-61	$C_2H_5O-CH_2-CH_2-OCH=CHPO(NC_5H_{10})_2$	Dipiperide of β -ethoxyethoxy- vinylphosphonic acid	185(2 mm)	1.506 ^c	1.0851	46	54	0	91
AP-36	$C_6H_5O-CH=CHPO(NC_5H_{10})_2$	Dipiperide of β -phenoxyvinyl- phosphonic acid	202(1 mm)	1.5528	1.1193	44	56	0	84
AP-37	$C_6H_5-CH=CHPO(NC_5H_{10})_2$	Dipiperide of β -phenylvinyl- phosphonic acid	M. p. 135—136	—	—	45	55	0	87

Table 1 contains the tetraethyldiamides of β -ethoxyvinylphosphonic, β -butoxyvinylphosphonic, β -ethoxyethoxyvinylphosphonic, and β -phenylvinylphosphonic acids.

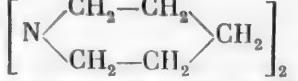
On addition of 2% of the tetraethyldiamides of β -ethoxyvinylphosphonic and β -butoxyvinylphosphonic acids to MS-20 oil the thermooxidative stability is increased by 23-25 minutes, while lacquer deposition falls to 5% (AP-58, AP-59).

The tetraethyldiamides of β -ethoxyethoxyvinylphosphonic and phenylvinylphosphonic acids produced a greater improvement in the antioxidant properties of the oil: T_{250} rose by 61-65 minutes, and lacquer deposition fell to 1-0% (AP-19, AP-22).

It was shown earlier that introduction of phenyl radicals and ethoxy groups into unsaturated phosphonic esters increases their antioxidant activity.

The results of the present investigation confirm that the presence of phenyl and ethoxy ($\text{CH}_2-\text{CH}_2-\text{O}$) groups in tetraethyldiamides of unsaturated phosphonic acids improve the antioxidant properties of the oil considerably.

The tetrabutyldiamides of unsaturated phosphonic acids have better antioxidant properties than the tetraethyldiamides (Table 2). The most effective is the tetrabutylamide of β -ethoxyvinylphosphonic acid (AP-21), which increases T_{250} by 70 minutes and lowers lacquer deposition to 0. The dipiperidides of unsaturated phosphonic acids (Table 3) have even better antioxidant properties than tetraethyldiamides and tetrabutyldiamides. Introduc-

tion of the dipiperide radical  sharply raises the antioxidant properties of the compounds. For example, the compounds AP-34, AP-35, AP-36, and AP-37 raised the thermooxidative stability of MS-20 oil to 84-103 minutes, the lacquer deposition fell to 0.

It should be noted that tetraalkyldiamides, and especially piperidides, of unsaturated phosphonic acids have better antioxidant properties than the esters of unsaturated phosphonic acids.

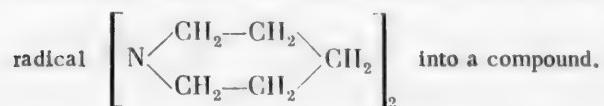
TABLE 4
Effect of Amide-Radical Length on the Antioxidant Properties of MS-20 Oil

Code mark	Formula	Engine prop. of MS-20 oil + 2% of compound, GOST 5737-53 (%)			Thermooxidative stability at 250° by the Papok method (min)
		E II	WF PΦ	L II	
AP-18	$\text{C}_6\text{H}_5-\text{CH}=\text{CHPO}[\text{N}(\text{CH}_3)_2]_2$	50	50	0	76
AP-22	$\text{C}_6\text{H}_5-\text{CH}=\text{CHPO}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	47	53	0	88
AP-33	$\text{C}_6\text{H}_5-\text{CH}=\text{CHPO}[\text{N}(\text{C}_3\text{H}_7-\text{n.})_2]_2$	45	55	0	69
AP-31	$\text{C}_6\text{H}_5-\text{CH}=\text{CHPO}[\text{N}(\text{C}_4\text{H}_9-\text{n.})_2]_2$	50	50	0	63

The following facts are also noteworthy: introduction of phenyl and phenoxy groups into tetrabutyldiamide and dipiperide compounds in the place of alkyl radicals does not improve the antioxidant properties, as is the case with the tetraethyldiamides and in esters of unsaturated phosphonic acids [1]; in the tetraethyldiamides and tetrabutyldiamides the antioxidant properties improve somewhat with increase of the length of the hydrocarbon radical in the $[\text{NR}_2]_2$ group from C_1 to C_2 , while further increase of the radical chain to C_4 lowers the antioxidant properties (Table 4).

SUMMARY

1. Of the compounds investigated, the dipiperidides of unsaturated phosphonic acids have the best antioxidant properties; the antioxidant properties are improved sharply by the introduction of the dipiperidine radical



2. Introduction of phenyl and phenoxy groups improves the antioxidant properties of tetraethyldiamides but has no influence in the case of tetrabutyldiamides or dipiperidides.

3. In tetraethyldiamides and tetrabutyldiamides the antioxidant properties diminish with increase of the hydrocarbon radical length in the $[\text{NR}_2]_2$ group from C_2 to C_4 .

4. Tetraalkyl diamides and piperidides of unsaturated phosphonic acids have better antioxidant properties than the esters of unsaturated phosphonic acids.

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THE ROLE OF CATALYZING ADDITIVES IN THE PRODUCTION OF FATTY ACIDS AND ALCOHOLS BY DIRECT OXIDATION OF PARAFFINIC HYDROCARBONS

Ya. B. Chertkov

After the production of monocarboxylic acids by direct oxidation of normal paraffins had been effected under industrial conditions, a new process was introduced for the production of alcohols of high molecular weight [1, 2].

Apart from other factors, the course of the processes is influenced by catalyzing additives, the role of which in many respects differs from the accepted role of "classic" catalysts.

Our investigations of the oxidation of paraffinic hydrocarbons for the production of acids and alcohols have led to a hypothesis concerning the role of catalyzing additives, based on studies of the formation mechanism of the required reaction products.

As is known, the optimum temperature for the production of acids is 105–115°, and the yield does not exceed 60% calculated on the hydrocarbons oxidized. For alcohols the temperature is 165–175°, and the yield may exceed 70%. In the "acid" process a certain amount of alcohol is formed, and in the "alcohol" process, a small amount of acids.

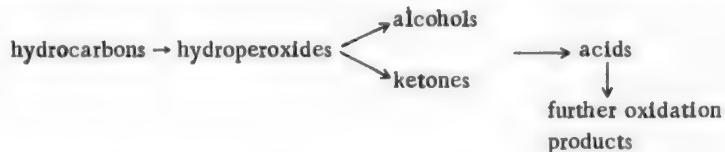
It is significant that despite the different reaction conditions with regard to duration, temperature, amount of air, and quite different catalyzing additives, in the alcohols formed the number of carbon atoms in the chain is close to that in the original hydrocarbons, whereas the acids are of different compositions: from formic acid to acids with the same number of carbon atoms as in the original hydrocarbon. The oxidation product generally contains, in definite proportions, the entire range of monocarboxylic acids which can be obtained from a hydrocarbon molecule with the given chain length.

Comparison of the oxidation products of paraffinic hydrocarbons with molecular weights in the 1000–300 range revealed certain differences in the proportions of acids of different molecular weights formed [3].

The fact that acids are formed in the oxidation process with extensive degradation of the original hydrocarbon molecule, but no such degradation occurs in the formation of alcohols, indicates that the mechanisms of their formation differ in principle.

Literature data would suggest that the difference between the mechanism of alcohol and acid formation is determined by their location in the chain of consecutive conversions.

For example, many workers [4–7] postulate the following scheme of hydrocarbon oxidation:

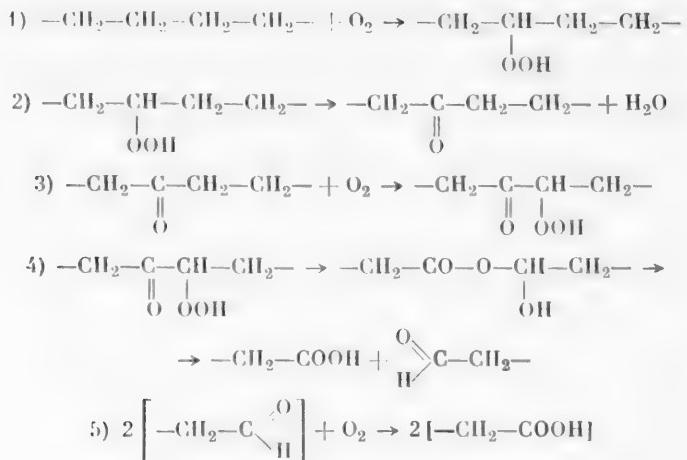


It is considered that the oxidation of alcohols may also lead to formation of acids by the scheme [8–11]



However, these schemes cannot account for the simultaneous formation of acids differing in molecular weight, and of alcohols of the same molecular weight.

According to one working hypothesis [12] acids are formed through a system of dihydric peroxides according to the scheme



By this scheme, acids of different molecular weight should be formed. However, it postulates the presence of considerable amounts of substances with carbonyl groups in the oxidation product, which is not found to be the case. Moreover, under these conditions the oxidation of aldehydes to acids proceeds to a very limited extent, because processes of oxidative condensation of aldehydes to resins develop at a much higher rate. Finally, it is difficult to explain the formation of formic acid, which is always formed in fairly large quantities, by these schemes.

We shall not consider other hypotheses, which provide even less adequate explanations of the mechanism of the formation of alcohols and acids under industrial conditions.

We studied the oxidation products of normal alcohols (nonanol, decanol, undecanol) formed under "acid" conditions. The alcohols were virtually unoxidized and did not undergo any changes. Therefore, alcohols could not be the sources of acids. In "alcohol" conditions, on the other hand, the alcohols were 25-50% oxidized, depending on the molecular weight.

Monocarboxylic acids, with the same number of carbon atoms in the chain as the original alcohols, were isolated and characterized as the principal oxidation products. It is clear that the acids present in the oxidation products could not have caused the existence of a range of different acids. Decanal was oxidized under the same conditions; it was 86-90% converted into a resinous mass which could not be distilled. It follows that aldehydes were not the source of acids either.

The remaining alternative was to study the thermal decomposition products of the monohydric hydroperoxide under conditions similar to those used in the production of acids and alcohols.

A concentrate of n-undecane hydroperoxide containing up to 80% of the pure hydroperoxide was prepared by a method described by Ivanov [13]. Investigation of the concentrate showed that the rest of it consisted of condensation products, separation of which resulted not in enrichment of the concentrate but partial breakdown of the hydroperoxide in it.

The concentrate of n-undecane hydroperoxide in the form of a 6.5% solution in n-undecane in the form of 20, 10, and 5% solutions in naphthalene, which proved to be quite inert under the given conditions, was subjected

to heat treatment with and without catalyzing additive in a reactor under conditions which reproduced the "acid" and "alcohol" regimes, except that nitrogen previously freed from traces of oxygen was passed instead of air through the reaction mass.

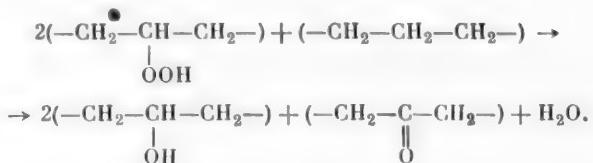
The products formed by thermal decomposition of the hydroperoxide were extracted and analyzed. They contained only traces of acids, and consisted mainly of alcohols and compounds containing the carbonyl group.

Thus, monohydric hydroperoxides likewise were not the main source of acids of different molecular weights. The principal products of the thermal conversion of the hydroperoxide were monohydric alcohols and carbonyl compounds. We may add that acids with long chains could not have been the source of acids with shorter chains, as has been believed by many workers, under the conditions of acid or alcohol formation.

For example, oxidation of stearic acid at 175° yielded a small quantity of hydroxy acids. 97% of the stearic acid was recovered unchanged from the oxidation product.

We formulated the following hypothesis [14] on the basis of extensive experimental data. Under "acid" and "alcohol" conditions the primary oxidation products of n-paraffins are monohydric hydroperoxides. The peroxide group may be attached at any carbon atom of a CH_2 group. Thermal decomposition of a hydroperoxide in which the peroxide group is adjacent to a methyl group leads to formation of an alcohol and formaldehyde, or an aldehyde and methanol, or a ketone and water. In the first two cases, the alcohol and aldehyde contain one carbon atom less in the chain than the original hydrocarbon. The ketone would have the same chain as the original hydrocarbon.

Some investigators have reported the formation of a mixture of secondary alcohols and ketones with the same number of carbon atoms as the hydrocarbon [15]. The presence of ketones is sometimes regarded as the result of interaction of two hydroperoxide molecules with a hydrocarbon molecule, with formation of two alcohol molecules, a ketone molecule, and water, according to the scheme:



It is possible that, in accordance with the conditions, both these schemes representing the thermal conversion of monohydric hydroperoxides, which do not yield acids directly, may be valid.

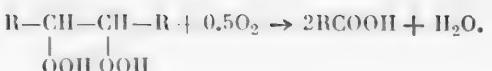
The rate of thermal conversion of monohydric hydroperoxides must increase with the temperature. At lower temperatures the peroxidation of monohydric to dihydric hydroperoxides would compete with this reaction. The second peroxide group is formed at a neighboring carbon atom in the α position relative to the first, which acts as the initiator [13]. Dihydric hydroperoxides are extremely unstable thermally, and decompose at relatively low temperatures in an oxidizing medium with formation of two molecules of acid and a molecule of water.

Since the work of Ivanov [13], who was one of the first to note the possible existence of dihydric peroxides and who isolated and characterized some of them, considerable numbers of new dihydric hydroperoxides have been prepared and investigated, and their presence in oxidation products has been detected [16-21].

The postulated mechanism for the formation of acids by thermal decomposition of dihydric hydroperoxides may be confirmed by the following results. We studied the composition of acids formed by oxidation of n-dodecane, n-tridecane, n-hexadecane, and n-octadecane under "acid" conditions.

From the oxidation products of each of the individual hydrocarbons acids were isolated and characterized, from formic up to the highest acids with the same number of carbon atoms in the molecule as in the original hydrocarbon. Acids of different molecular weights could have been formed only if the rupture of the carbon bonds in the hydrocarbon molecule was equally probable at any point.

If the suggested mechanism is valid, acids with half the number of carbon atoms of the original hydrocarbon should be formed in the greatest amount. If a symmetrical dihydric hydroperoxide is formed, it would decompose into two acid molecules of equal molecular weight.



In our case the fraction containing acids with approximately one-half the carbon atoms of the original hydrocarbon chain comprised 45-55% of the total.

In the light of this theory concerning the formation mechanism of acids and alcohols, we studied the role of catalyzing additives used under industrial conditions: potassium permanganate for the "acid" process, and boric acid for the "alcohol" process.

Alekseevskii [22] reported that active manganese dioxide is obtained as a by-product in the oxidation of organic substances by permanganates and manganates. It seems that in presence of manganese salts the oxidation of organic substances is intensified by active oxygen of manganese dioxide.

Schemes have been suggested for the formation of acids by oxidation of hydrocarbons in which it is postulated that the process is effected under the catalytic influence of manganese salts, which act as carriers of active oxygen in the form of manganese dioxide [23].

It was observed that Fe and Mn naphthenates are very active accelerators of peroxide formation [24]. In presence of 0.08% of Mn naphthenate more peroxide is formed (14 times as much) as in the oxidation of hydrocarbons under identical conditions but without the additive. It follows that Mn compounds favor the initial formation of peroxides.

It is now insufficient to characterize the role of KMnO_4 as merely that of a substance which accelerates peroxide formation, or a carrier of active oxygen which oxidizes the hydrocarbon molecules to acids. With the use of KMnO_4 catalyst it has been possible to effect a directed process in which fatty acids are formed as the main reaction products. This means that by its participation in the reaction KMnO_4 favors formation of peroxides which yield mainly acids as primary products in oxidative decomposition.

The directed process can be effected only if all other processes which lead to the formation of other oxidation products are suppressed to a considerable extent.

In our opinion, the manganese dioxide formed by decomposition of KMnO_4 , being a carrier of active oxygen, accelerates the peroxydation of monohydric to dihydric hydroperoxides at relatively low temperatures.

Thus, in presence of KMnO_4 the selectivity of the process with regard to formation of monocarboxylic acids as the principal reaction products is determined by: 1) favorable conditions for peroxydation of monohydric to dihydric hydroperoxides, 2) decomposition of dihydric hydroperoxides with formation of acids, and 3) high resistance of the acids to thermal oxidation under the reaction conditions.

At the temperature of the "alcohol" process (165-175°) the rate of thermal decomposition of monohydric hydroperoxides is incomparably greater than at the temperature of the "acid" process. Therefore, their peroxydation is possible only to a limited extent. This possibility is reduced to a minimum in oxidation by a gaseous mixture in which the amount of oxygen by weight is sharply lowered. Under these conditions, despite the higher process temperature, KMnO_4 has no catalytic influence on the course of the reaction.

The presence of KMnO_4 in the reaction zone in oxidation of n-octadecane and other individual hydrocarbons did not introduce any selectivity characteristics into the process.

An interesting fact is that the peroxide number of the oxidation product formed at 120° in presence of KMnO_4 was double that of the product formed at 175°. This also serves to confirm the proposed mechanism of acid formation and the role of KMnO_4 as a catalyzing additive.

Boric acid is the best catalyzing additive in the "alcohol" process. In contrast to KMnO_4 , 0.2% of which is added to hydrocarbons, the optimum amount of boric acid is 4-5%. The considerable difference between the amounts of catalyzing additives in itself indicates that their roles in the oxidation of hydrocarbons are different in principle.

The information available on the use of boric acid as a catalyzing additive is very limited.

At 350° in presence of boric acid complete dehydration of primary, secondary, and tertiary alcohols occurs [25].

In a paper by Bell et al. [26] it is described how the inner walls of the reactor were treated with boric acid in the oxidation of branched hydrocarbons. According to these authors, boric acid restricted the extent of oxidation and intensified its initial period. On addition of 1% of boric acid to coal subjected to distillation the tar yield fell from 5 to 3.5%. The tar was not dark brown and viscous as usual, but liquid and yellow or yellow-brown in color. The yield of low-viscosity oils was considerably higher, and that of substances insoluble in benzene and of phenols was less [27].

Boric acid is fairly easily and completely esterified by alcohols, especially primary and secondary alcohols of the aliphatic series. At the same time, these esters are decomposed almost completely into alcohols and boric acid by treatment with hot water. Borate esters of alcohols are thermally stable in an oxidizing medium, and boil at considerably higher temperatures than the corresponding alcohols.

Scipioni [28, 29], who used boric acid as a catalyzing additive in the "alcohol" process, concluded that increase of the boric acid concentration accelerates peroxide formation.

This completes the available information on the catalytic effects of boric acid.

It is known that in presence of boric acid the oxidation of normal paraffins is extremely selective, with predominant formation of alcohols. The process begins to develop when a temperature of 165-175° is reached, and is complete in 2-4 hours. In presence of boric acid the amount of alcohols formed is 2-3 times the amount formed in oxidation without boric acid.

Under these conditions two different processes play an important role. The first process results in formation of monohydric hydroperoxides and the products of their thermal decomposition. In the second process the alcohols formed are combined in the form of borate esters. The more similar the rates of these reactions, the more effective and selective the process is. Since the rates of hydrocarbon oxidation and, even more so, of subsequent oxidative conversions, are usually higher than the rate of alcohol esterification, it has been suggested that the oxidation rate should be regulated by limiting the oxygen concentration in the gaseous mixture entering the reactor. Thereby it proved possible to avoid secondary and more extensive oxidative conversions leading to the formation of resinous oxygen-containing by-products, to decrease the formation rate of monohydric hydroperoxides, and thus to prevent almost completely their peroxidation to dihydric hydroperoxides. In this way the amount of acids formed in the "alcohol" process was reduced to 5-7% of the total oxygen compounds.

Under these conditions the alcohols formed by thermal decomposition of monohydric hydroperoxides are combined fairly rapidly and almost completely in the form of borate esters, which are thermally stable, do not undergo any changes, and do not influence the development of hydrocarbon oxidation. The alcohols were, in a sense, "protected" against further conversion in the reaction zone. At the same time, because of the continuous "removal" of alcohols from the reaction the latter develops in such a way that the thermal decomposition of hydroperoxides proceeds predominantly with alcohol formation. This concept of the catalytic role of boric acid in the "alcohol" process was based on extensive experimental data.

It is evident that, in contrast to KMnO₄, boric acid does not intensify the oxidation process but, on the contrary, retards it somewhat, "protecting" and thereby "removing" the decomposition products of monohydric hydroperoxides (alcohols) from the reaction zone.

An interesting fact is that the role of boric acid described above is specific for normal paraffins only. Boric acid does not have this influence on the oxidation of hydrocarbons with other structures; this should be attributed primarily to differences in the chemical processes and esterification rates of the hydroxylic compounds formed.

SUMMARY

The foregoing account of the role of catalytic additives used in oxidation of paraffins to acids and alcohols indicates that great possibilities exist for development of new selective processes of hydrocarbon oxidation for the production of oxygen-containing compounds valuable in the national economy.

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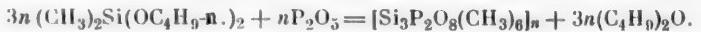
REACTIONS OF ALKYLALKOXY SILANES WITH PHOSPHORIC ANHYDRIDE

A. P. Kreshkov and D. A. Karateev

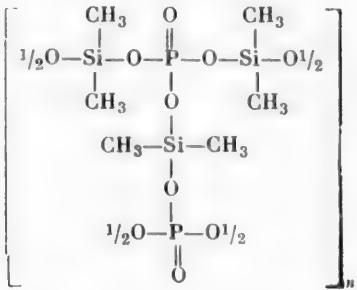
Many investigators have studied the reactions of alkylalkoxy silanes with PCl_3 [1, 2], PBr_3 [2-5], PCl_5 [6, 7] and POCl_3 [2, 8].

Reactions of alkylalkoxy silanes with phosphoric anhydride are not described in the literature.

The present paper deals with a study of the reactions of certain mono- and difunctional alkylalkoxy silanes with phosphoric anhydride. In the reaction of dimethyldi-n-butoxysilane with phosphoric anhydride we obtained an organic compound of silicon and phosphorus of the composition $[\text{Si}_3\text{P}_2\text{O}_8(\text{CH}_3)_6]_n$ or $\{[(\text{CH}_3)_2\text{Si}]_3(\text{PO}_4)_2\}_n$. Its formation may be represented by the equation:



Its presumed structural formula is

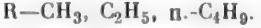


The synthesized compound contains alternating $\text{Si}-\text{O}-\text{P}$ bonds. We therefore described it as a dimethylpolysiloxane phosphate [9]. This compound was prepared by Voronkov and Zgonnik by the reaction of R_2SiX_2 or RSiX_3 (where X is halogen or OCH_3) with solid phosphoric acid [10].

We also developed a new method for preparation of tris(trimethylsilyl) phosphate, based on the reactions of trimethylalkoxy silanes with phosphoric anhydride:



where



With $(\text{CH}_3)_3\text{SiOCH}_3$ as the starting material, the yield of tris(trimethylsilyl) phosphate was 10%, with $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ it was 40-50%, and with $(\text{CH}_3)_3\text{SiOC}_4\text{H}_9$, 60-70% of the theoretical.

Tris(trimethylsilyl) phosphate and its analogs were also prepared by reactions of trialkylalkoxy and halo silanes with phosphoric acid or its esters, and of hexaalkyl disiloxanes with phosphoric anhydride [10, 11].

Our proposed method for synthesis of tris(trialkylsilyl) phosphates is new, and has not been described in the literature. The method is simple, rapid, and gives pure products in high yields. In the reaction of dimethyl-diethoxysilane with phosphoric anhydride a white crystalline substance with the composition $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$ was isolated. The same compound was obtained by the action of dimethyl diethoxysilane on phosphorus oxychloride.

EXPERIMENTAL

The starting materials for the preparation of the organic silicon and phosphorus compounds were dimethyl-diethoxysilane, dimethyl-di-n-butoxysilane, trimethylmethoxysilane, trimethylethoxysilane, and trimethyl-n-butoxysilane.

Dimethyl diethoxysilane and dimethyl-di-n-butoxysilane were prepared from the corresponding chlorosilanes and anhydrous alcohols by methods described in [12, 13].

Trimethylmethoxy-, trimethylethoxy-, and trimethylbutoxysilane were prepared by a method based on the reaction of aniline with trimethylchlorosilane with subsequent interaction of the $(\text{CH}_3)_3\text{SiNHC}_6\text{H}_5$ formed with the corresponding anhydrous alcohol [14]. The yields of trimethylalkoxy silanes were 70–80% of the theoretical. The physical constants of the starting compounds corresponded closely to the values given in the reference literature.

The physical constants of the alkylalkoxy silanes are given in the table.

Physical Constants of Alkylalkoxy Silanes

Formula of compound	Boiling point (in °C)	d_4^{20}	n_D^{20}
$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	111–112	0.893	1.3860
$(\text{CH}_3)_2\text{Si}(\text{OC}_4\text{H}_9\text{-n.})_2$	187–188	0.847	1.4060
$(\text{CH}_3)_3\text{SiOCH}_3$	57.2–57.8	0.759	1.3690
$(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$	75–76	0.7547	1.3755
$(\text{CH}_3)_3\text{SiOC}_4\text{H}_9\text{-n.}$	124–125.5	0.781	1.3932

Reaction of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ and P_2O_5 . 25.0 ml (0.150 mole) of freshly prepared $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ was put in a round-bottomed 100 ml flask fitted with a reflux condenser. 7.1 g (0.05 mole) of P_2O_5 was then added gradually during 15–20 minutes. After the addition of P_2O_5 the mixture was heated to the boil on an oil bath and boiled for 3 hours. Distillation of the reaction mixture yielded fractions containing diethyl ether and also phosphate esters. At temperatures above 200° the liquid frothed and a white precipitate of a substance containing silicon and phosphorus was deposited.

Reaction of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ and POCl_3 . 22.5 ml (0.135 mole) of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ was put in a round-bottomed flask fitted with a reflux condenser, and 12.3 ml (0.135 mole) of POCl_3 was then added gradually during 30 minutes; the mixture became appreciably warm and gaseous $\text{C}_2\text{H}_5\text{Cl}$ was evolved. The reaction mixture was boiled for 1–1.5 hours on an oil bath. Distillation of the resultant reaction mass yielded fractions containing diethyl ether and phosphoric acid chloro esters. On further heating to above 200° a white or slightly yellowish precipitate of a substance containing silicon and phosphorus was formed in the flask.

Analysis of the solid substances containing silicon and phosphorus, after they had been washed with alcohol and benzene, showed that the same product is formed in the reaction of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ with P_2O_5 and with POCl_3 .

For determination of phosphorus a sample of the substance was heated in excess of standard approximately 0.1 N NaOH solution, followed by titration of the excess alkali with 0.1 N HCl solution in presence of Methyl orange.

Silicon was determined by a photolorimetric method [12], and carbon and hydrogen were determined by microcombustion.

Analytical data for the solid products containing silicon and phosphorus are given below.

Found %: P 32.3, 32.5, 32.42; Si 7.42, 7.10, 7.24; H 1.32, 1.36, 1.46. $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$. Calculated %: P 32.60; Si 7.39; H 1.05.

The results of chemical analysis suggest that the inorganic silicon and phosphorus compound has the composition and structure: $\text{SiP}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ or $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$.

The fractions containing diethyl ether were redistilled with a dephlegmator; $(\text{C}_2\text{H}_5)_2\text{O}$ was collected in a flask cooled in snow, and identified (b. p. 35-36°, d_4^{20} 0.7203). The solid product $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$ was subjected to x-ray structural analysis. The photograph was taken in a Debye camera with $\text{Cu D } \phi = 0.6$ and $2R = 90.2$. The compound was found to have a crystalline structure (Fig. 1).



Fig. 1. X-ray photograph of the silicon and phosphorus compound.

Reaction of $(\text{CH}_3)_2\text{Si}(\text{OC}_4\text{H}_9)_n$ and P_2O_5 . 36.3 ml (0.15 mole) of $(\text{CH}_3)_2\text{Si}(\text{OC}_4\text{H}_9)_n$ was put in a round-bottomed 100 ml flask fitted with a reflux condenser, and 7.1 g (0.05 mole) of P_2O_5 was added gradually (during 15-20 minutes). The reaction mixture was then heated to the boil and boiled on an oil bath for 2.5 hours. Distillation of the reaction mass yielded fractions containing dibutyl ether and phosphate esters, and a small excess of the original $(\text{CH}_3)_2\text{Si}(\text{OC}_4\text{H}_9)_n$ (185-189°). When the mixture was heated to 260-270°, the liquid in the distillation flask frothed and a liquid pale yellow substance was formed, which thickened to a sticky yellow mass on cooling. The substance was sparingly soluble in organic solvents, but dissolved in dilute NaOH on heating. The substance was analyzed as described above for the compound $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$. However, because of the presence of Si-C bonds in the substance, it was first necessary to decompose a weighed sample by heating with excess concentrated H_2SO_4 to which a little concentrated HNO_3 had been added. The mixture of acids was evaporated off, and the SiO_2 formed was dissolved in 10 ml of 15% KOH solution, transferred to a 500 ml measuring flask, neutralized with H_2SO_4 solution in presence of phenolphthalein, and determined by the photo-colorimetric method [15].

The following average values were obtained by chemical analysis.

Found %: Si 22.85; P 17.32; C 19.09; H 5.50. $\text{Si}_3\text{P}_2\text{O}_8(\text{CH}_3)_6$. Calculated %: Si 23.12; P 17.00; C 19.77; H 4.98.

The analytical data for the substance correspond to the composition $[\text{Si}_3\text{P}_2\text{O}_8(\text{CH}_3)_6]_n$ or $\{[(\text{CH}_3)_2\text{Si}]_3(\text{PO}_4)_2\}_n$.

The molecular weight of the dimethylpolysiloxane phosphate was determined by the Rast method, the solvent used being benzoic acid, which has a high molecular depression (87.88°). According to these determinations, the substance had molecular weight 2550 ($n \approx 7$) on the day after it was prepared, and 2970 ($n \approx 8$) 2 months after synthesis.

Redistillation of the 141-143° fraction with a dephlegmator yielded $(n\text{-C}_4\text{H}_9)_2\text{O}$ of b. p. 141-142°; it was identified (d_4^{20} 0.771; $n^D 1.4031$).

Reactions of trimethylalkoxy silanes with phosphoric anhydride. Into a round-bottomed 100 ml flask fitted with a reflux condenser was put 0.2 ml of the trimethylalkoxy silane: trimethylmethoxy-, trimethylethoxy-,

or trimethyl-n-butoxysilane, and 14.2 g (0.1 mole) of P_2O_5 was added gradually (during 30-40 minutes) with continuous shaking of the flask. The reaction mixture was heated to the boil and boiled on an oil bath for 2 hours. The corresponding ethers were formed and evolved in all the experiments. The reaction mixture from each experiment was distilled under vacuum, the 94-98° fraction (6 mm) or the 110-117° fraction (12 mm) being collected. In the second distillation: the 96-97° fractions (6 mm) were collected. In the reaction of $(CH_3)_3SiOC_4H_9$ with P_2O_5 the yield of the pure product was 60-70% of the theoretical, calculated on the trimethylalkoxy silane taken. In the case of $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiOC_2H_5$ the yields were 10 and 40-50%, respectively. The pure tris(trimethylsilyl) phosphate was analyzed.

The analytical data are given below.

Found %: P 10.25, 9.94, 9.73; C 34.09, 34.20; H 8.12, 8.31. $[(CH_3)_3Si]_3PO_4$. Calculated %: P 9.85; C 34.36; H 8.76.

The molecular weight, determined cryoscopically in benzene, was 313.7; calculated 314.56. The constants were: d^{20}_4 0.962, $n^{20}D$ 1.4083.

Literature data: d^{20}_4 0.959, b. p. 232.6° or 97° (6 mm); $n^{20}D$ 1.4089 [11].

An interesting fact is that with a 6:1 molar ratio of alkylalkoxy silane to phosphoric anhydride, as indicated by the reaction equation, the process is less complete, and a considerable amount of the original alkylalkoxy silane remains. Therefore, a 2:1 molar ratio of alkylalkoxy silane to P_2O_5 was used.

When the mixture is distilled under normal pressure, very little tris(trimethylsilyl) phosphate is formed, as a white precipitate of an inorganic compound containing silicon and phosphorus is formed in the flask even at 160-200°.

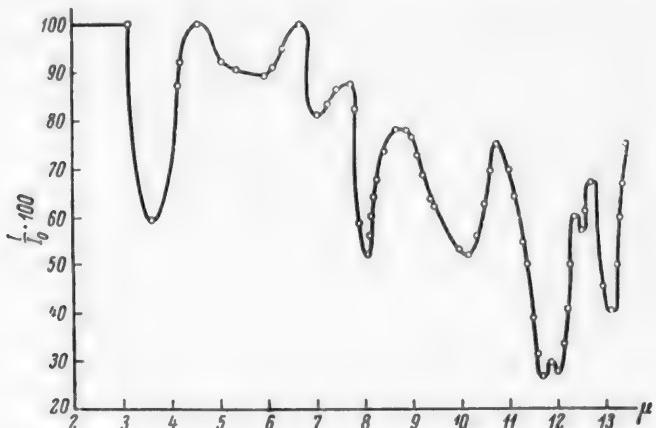


Fig. 2. Infrared spectrum of tris(trimethylsilyl) phosphate.

The infrared spectrum of tris(trimethylsilyl) phosphate was determined by means of the IKS-11 spectrograph with a sodium chloride prism. The substance was taken in the form of 10% solutions in carbon tetrachloride (up to 10 μ) and in carbon disulfide (above 10 μ). The absorption curve of tris(trimethylsilyl) phosphate is given in Fig. 2.

The infrared spectrum was interpreted on the basis of the results given in a number of publications [16-18].

According to these data the absorption maxima may be referred to the following groups and bonds: 3.6 μ and 7.08 μ (C-H in CH_3), 8.06 μ , 11.9 μ , and 13.1 μ [$Si(CH_3)_3$], 8.06 μ ($P=O$) and 10.18 μ ($P-O$). The absorption maxima for the $Si-C$ and $P=O$ bonds are very close to each other (the difference does not exceed 0.1 μ). The corresponding maxima therefore coalesced in the spectrum.

Trials showed that addition of our organic silicon-phosphorus compounds, such as dimethylpolysiloxane phosphate, to cement pastes, in amounts of 0.5-1% on the weight of dry cement, has a favorable effect on water absorption, compressive strength, and frost resistance of the cements.

SUMMARY

1. A compound containing silicon and oxygen, of the composition $\text{Si}(\text{PO}_3)_4 \cdot 2\text{H}_2\text{O}$ and with a crystalline structure, was isolated from the reaction products of dimethyldiethoxysilane with phosphoric anhydride or phosphorus oxychloride.
2. The reaction of dimethyldi-n-butoxysilane with phosphoric anhydride gives a compound of the composition $[\text{Si}_3\text{P}_2\text{O}_8(\text{CH}_3)_6]_n$ or $\{[(\text{CH}_3)_2\text{Si}]_3(\text{PO}_4)_2\}_n$, where n is 7 or 8.
3. A new method has been developed for the preparation of tris(trimethylsilyl) phosphate, based on the reaction of trimethylmethoxy-, trimethylethoxy-, or trimethyl-n-butoxysilane with phosphoric anhydride.

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EFFECT OF PRETREATMENT OF VEGETABLE RAW MATERIALS WITH ORGANIC SOLVENTS ON THE COURSE OF FORMATION AND YIELD OF FURFURAL

A. A. Shcherbakov and Yu. K. Yur'ev

At the All-Union Conference on the utilization of pentosan-containing raw materials held in October, 1955 [1] attention was drawn to the importance of research into the production of furfural and utilization of compounds obtained from it. An interesting possibility in this connection is the increase of furfural yields by preliminary treatment of the raw materials with solvents, for fuller utilization of the raw material and for decreasing losses of furfural due to resinification during hydrolysis.

In our previous paper [2] it was shown that addition of chloroform to raw material hydrolyzed by 10% sulfuric acid increases the crude furfural yield by 2% calculated on the air-dry material, or by 25% if the furfural yield by hydrolysis in absence of chloroform is taken as 100%.

It is known from the literature that in hydrolysis of tan wastes [3] and sunflower husks [4] by sulfuric acid under pressure the furfural content in the digester vapors increases rapidly at first, reaches a maximum, and then falls. It is also known that addition of neutral solvents has a significant influence on the course of hydrolysis of pentosan raw materials. Thus, Khristich [5] found that addition of benzene or toluene to the reaction mass increases the furfural yield by 10-15% over the yield obtained by the analytical method [6]; the additives accelerate the volatilization of furfural and, by dissolving the latter, rapidly isolate it from the action of the acid. Furfural yields are also increased by additions of benzene, diphenyl [7], or paraffin oil (to oat chaff) [8] to the raw materials. Sharkov [4] presented data on the influence of neutral solvents on depolymerization of cellulose by anhydrous hydrogen chloride at 20° and 43-75 atmos; some solvents (alcohols, ether, acetone, carbon tetrachloride, methylene chloride) accelerate depolymerization, and others (benzene, lignoine) retard it.

The effect of pretreatment of vegetable materials with organic solvents on the course of pentosan hydrolysis and furfural yields has not been studied previously. We studied this effect both under the conditions of analytical determination of furfural in hydrolysis of vegetable material with 12% hydrochloric acid (by the Tollens method), and in the laboratory preparation by our modification of the Adams method [2].

Our results showed that pretreatment of vegetable material with alcohol or ether increases the furfural yield in hydrolysis, whereas treatment with lignoine decreases it. The results of treatment with benzene, chloroform, and other solvents depend on the nature of the raw material, its pentosan content, nature of the solvent used, and the hydrolysis conditions, and indicate that physicochemical interaction takes place between the solvent and the vegetable material.

EXPERIMENTAL

In studies of the course of furfural formation by the hydrolysis of vegetable material with 12% hydrochloric acid by the standard method [6], the materials used were corn cob stalks, barley husks, oat chaff, rape wastes, millet, buckwheat, and sunflower husks, tomato and potato haulms, orache stalks, and pinewood sawdust. The end of hydrolysis was indicated by a negative test for furfural with aniline acetate. The furfural content of the distillate was determined by the bromide-bromate method [9].

TABLE I
Course of Furfural Formation in Hydrolysis of Vegetable Raw Materials by 12% Hydrochloric Acid After Pretreatment with Solvents

Plant material	Pentosan content (%)	Solvent	Am. distillate of furfural (ml) yield (%)	hydrolysis time (hours)				Total furfural yield (%)	Yield increase (%) on raw mat.	Yield (%) on raw mat. on furfural			
							1	2	3	4			
Sunflower husks	26.15	No pretreatment	68	12.1	62	1.78	60	1.44	60	0.2	15.52	—	—
		Ether	65	8.43	65	3.93	62	1.78	70	0.24	14.38	1.14	7.3 **
		Alcohol	70	11.1	73	3.16	68	1.44	70	0.24	15.94	0.42	2.7
		Chloroform	60	10.35	64	4.50	62	1.60	70	0.20	16.65	1.13	7.2
		Carbon tetrachloride	60	4.62	63	7.71	65	3.61	70	0.54	16.48	0.96	6.1
		Benzene	62	8.9	64	3.62	62	1.70	70	0.2	14.42	1.10	7.1 **
		Ligroine	62	7.1	62	5.21	60	1.50	70	0.1	13.91	1.61	10.4 **
		Vaseline oil	56	8.45	60	5.84	60	1.83	67	0.32	16.44	0.92	5.5
		No pretreatment	70	7.5	60	6.0	60	1.50	66	0.15	15.45	—	—
		Ether	68	10.5	60	3.45	65	1.40	68	0.17	15.52	0.37	2.4
Buckwheat husks	26.23	Alcohol	60	10.33	67	3.21	60	1.55	68	0.22	15.31	0.16	1.1
		Chloroform	63	6.8	67	7.46	65	1.62	67	0.27	16.15	1.00	6.6 **
		Benzene	68	10.2	63	3.0	60	0.69	65	0.26	14.15	1.00	6.6 **
		Ligroine	60	8.67	60	2.95	66	0.56	68	0.19	12.37	2.78	18.3 **
		No pretreatment	68	8.4	60	2.3	60	1.60	65	0.15	12.45	—	—
Millet husks	20.20	Ether	62	9.29	65	2.4	60	1.62	68	0.24	13.55	1.1	8.8
		Alcohol	62	9.5	60	2.33	65	1.48	66	0.17	13.48	1.03	8.2
		Chloroform	62	8.19	60	3.10	60	1.61	60	0.30	13.2	0.75	6.2
		Dichloroethane	63	7.0	55	5.55	67	1.81	65	0.00	14.36	1.91	15.3
		Carbon tetrachloride	56	7.86	64	5.15	66	0.85	68	0.10	13.96	1.51	12.1
		Benzene	61	8.4	56	2.58	66	1.42	65	0.23	12.63	0.18	1.4 **
		Ligroine	60	6.8	68	2.39	57	1.42	68	0.23	10.84	1.61	12.4 **
Vaseline oil		Vaseline oil	53	8.7	61	3.21	56	1.34	61	0.25	13.50	1.05	8.4

* Calculated on air-dry material.

** Furfural yield decreased in these experiments.

TABLE 1 (Continued)

Plant material	Pentosan content (%)	Solvent		hydrolysis time (hours)				Yield increase (%)	Yield on raw material (%)
				1	2	3	4		
Corn cob stalks (unnamed varieties)									
38.64		No pretreatment							
	Ether			65	15.4	60	4.9	70	1.8
	Alcohol			60	15.1	66	5.9	65	2.5
	Chloroform			63	14.94	62	5.88	60	1.73
	Dichloroethane			55	14.99	65	9.88	65	1.97
	Carbon tetrachloride			64	13.54	60	6.7	67	2.6
	Vaseline oil			68	11.85	60	9.9	66	1.98
	No pretreatment			60	15.83	61	6.03	69	1.72
29.23				60	14.0	65	2.14	66	0.6
	Ether			60	7.91	65	8.6	63	1.2
	Alcohol			65	12.49	60	4.76	60	0.16
	Chloroform			60	9.52	60	8.5	70	0.35
31.23				55	12.6	60	3.5	72	1.7
19.07				58	8.62	60	1.8	60	0.7
24.38				60	8.80	60	4.5	70	0.55
23.80		No pretreatment		70	7.80	68	4.8	67	1.30
21.29				63	6.50	60	4.7	70	1.15
12.40				64	2.50	60	2.1	70	0.4

The results, given in Table 1, show that most of the furfural is formed and liberated from the reaction medium during the first hour of distillation (some, but considerably less, is formed during the second hour); this agrees with the data of Serchel' [3] and Primo [4].

There is no direct relationship between pentosan content and furfural yield.

Thus, with equal pentosan contents in buckwheat and sunflower husks (26.23 and 26.15%), the furfural yields in the first hour of distillation were 7.5 and 12.10%, respectively. The pentosan content of oat chaff is 31.23%, and of barley husks, 29.23%, while the furfural contents in the distillate during the first hour were 12.6 and 14.0% respectively. The same is found for rape wastes, and potato and tomato haulms. In hydrolysis of buckwheat husks, potato haulms, pinewood sawdust, and orache stalks, the maximum furfural yield extends somewhat uniformly over the first two hours of distillation. Near the end of hydrolysis the furfural content of the distillate becomes almost the same in all cases (0.2-0.3%) regardless of the pentosan contents of the raw materials.

Variations of the furfural content of the distillate with the time of hydrolysis of plant tissues reflect the reactions of monosaccharide (pentose) formation from polysaccharides (pentosans) and decomposition of the pentoses formed into furfural and other substances [10].

It follows from Table 1 that the pentosans hydrolyzed most easily are those in corn cob stalks, barley husks, oat chaff, and sunflower husks (15.4-12% of furfural in the distillate during the first hour, and 4.90-1.78% during the second).

The hydrolysis of pentosans in buckwheat husks, tomato and potato haulms, orache and pinewood sawdust proceeds with more difficulty — during the second hour of distillation from 50 to 85% of the amount of furfural liberated during the first hour enters the distillate.

It should be noted that Pryanishnikov and Mashevitskaya [11], who studied the accumulation of reducing substances in solutions formed after hydrolysis of vegetable materials with 2% hydrochloric acid, also found that pentosans in corn cob stalks are hydrolyzed more easily, and those in straw more easily still, than the pentosans of sunflower husks.

In a second series of experiments, conducted under the same conditions, we studied the influence of pre-treatment of the vegetable materials with organic solvents on the course of furfural formation. 1 g of the shredded material with 10 ml of solvent was put in a flask and left for 24 hours. At the end of this period 100 ml of 12% hydrochloric acid was added, and the furfural was distilled as indicated above.

The results of these experiments, given in Table 1, show that pretreatment of the raw materials with alcohol, ether, chloroform, benzene, ligoine, dichloroethane, carbon tetrachloride, and vaseline oil influences both the yield of furfural and the course of its formation.

In most instances treatment with alcohol or ether increases the furfural yield owing to some increase of the rate of pentosan hydrolysis during the second hour of the process. Thus, sunflower husks not treated with alcohol yield 12.1 % of furfural during the first hour and 1.78% during the second, whereas after alcohol treatment the yield in the first hour is 11.1%, and in the second, 3.16% of furfural. The furfural yield increases by 0.42% on the raw materials or by 2.7% on furfural.

The same is found for barley husks and corn cob stalks. In consequence the total furfural yield from these materials increases by 2.4% after alcohol treatment, and by 6.45% after ether treatment, as compared with the yields in absence of solvents.

When sunflower husks are treated with ether, the increase in the pentosan hydrolysis rate during the second hour does not compensate for the decrease in the first hour, and the total furfural yield decreases.

With millet and buckwheat husks the increase in the furfural yields after treatment with alcohol or ether is due to intensified pentosan hydrolysis during the first hour.

Treatment of sunflower, buckwheat, and millet husks with ligoine (b. p. 90-105°) lowers the hydrolysis rate so much that the total furfural yields decrease by 10.4, 18.3, and 12.4%, respectively as compared with the yields in absence of ligoine. Benzene treatment also lowers the yields of furfural from sunflower and buckwheat husks by 6.85% as compared with yields in absence of benzene.

Chloroform treatment raises the furfural yields from sunflower, buckwheat, and millet husks, corn cob stalks, and barley husks by 7.2, 6.6, 6.2, 8.3, and 8.4 %, respectively. The increase of the total furfural yield in these cases is due to an increase of the furfural concentration in the distillate during the second hour of hydrolysis.

Treatment of millet husks and corn cob stalks with dichloroethane increases the furfural yields by 15.3 and 4.7%, respectively.

Carbon tetrachloride treatment of sunflower and millet husks and corn cob stalks increases the furfural yields by 6.1, 12.1, and 8.6%, respectively.

Vaseline oil treatment of sunflower and millet husks and corn cob stalks raises the furfural yields by 5.5, 8.4, and 7.6%, owing to increased hydrolysis rates both in the first and in the second hours of the process.

These results show that the same solvents have different effects on the course of hydrolysis of pentosans in different vegetable materials by 12% hydrochloric acid. However, in all cases the process is more uniform in presence of solvents, owing to some decrease of the hydrolysis rate during the first hour, because the solvent has to be displaced from the surface of the vegetable tissue by the hydrolyzing agent, so that a somewhat greater proportion of the pentosans are hydrolyzed during the second hour. In some cases this leads to a decrease and in others to an increase of the total furfural yield; undoubtedly this is due not only to differences in the hydrolyzability of the polysaccharides, but also to physicochemical interaction of some of them with the solvents (alcohol and ether). It seemed likely that treatment of sunflower husks with ether should lower the hydrolysis rate of the pentosans during the first hour only slightly, because of the probable rapid distillation of the ether. In reality it was found that ether is removed with difficulty from this vegetable material, and lowers the pentosan-hydrolysis rate during the first hour to a greater extent than alcohol, chloroform, or benzene.

Ligroine, having wetted and penetrated the plant tissue, prevents access of acid not only to the surface (as in the case of vaseline oil) but also into the depth of the tissue, and hinders liberation of the furfural already formed. Both these factors lower the rate of pentosan hydrolysis and considerably decrease the total furfural yield.

Pretreatment of vegetable raw material with benzene also lowers the total furfural yield; in some cases owing to a decrease of the rate of pentosan hydrolysis during the first hour of the process (sunflower husks, corn cob stalks, barley husks), and in some cases during the second hour (buckwheat husks).

In the third series of experiments we studied the hydrolysis of corn cob stalks (unnamed varieties) and a sunflower and millet husks with 10% sulfuric acid by our modification of the Adams method [2] (with and without steam distillation), after treatment with vaseline oil, solar oil Diesel fuel, carbon tetrachloride, and dichloroethane.

500-1500 g lots of the shredded material were put in a 12-liter copper flask fitted with a downward condenser, and solvent (25% on the weight of the material) was added. The contents were stirred thoroughly for 10 minutes, and left to stand for 48 hours and half an hour, respectively in parallel experiments. A 10% solution of sulfuric acid was then added, followed by common salt [2], and the distillation was continued for 6 hours. The furfural contents of the distillates collected during each hour were determined. If the organic solvent was also distilled off, its furfural content was determined by weight after evaporation of the solvent.

After each 580 ml of distillate had been collected, an equal volume of acid was added dropwise into the flask (without interruption of the process). If steam was passed into the flask, additional acid was not introduced, and the distillation rate was three times as high.

The results in Table 2 show that pretreatment of large quantities of the raw materials with carbon tetrachloride, dichloroethane, Diesel fuel, or vaseline or solar oils increases the furfural yield. After 48 hours of pretreatment the yield of furfural from corn cob stalks increases (without steam distillation) on the average by 5.42% from sunflower husks by 3.3% and from millet husks by 3.5% calculated on the air-dry material, or by 43.0, 46.7, and 59.7%, respectively on the furfural yields obtained without the use of solvents. The furfural yields are increased considerably both during the first and during the second hours of pentosan hydrolysis.

If the material is treated with solvent for half an hour, the furfural yield (without use of steam) increases on the average by 2.90% calculated on the air-dry material, or by 43.4% on the yield of furfural, the least increase of the yield being obtained with solar oil (2.07% or 35.2%) and the greatest with dichloroethane (3.96% or 67.3%). With steam distillation, the yield of furfural from corn cob stalks increases on the average by 3.1% on the raw material or 21% on the furfural yield, and from sunflower husks, by 2.71 and 30.6%, respectively.

TABLE 2
Course of Furfural Formation in Hydrolysis of Vegetable Raw Materials by 10% Sulfuric Acid After Pretreatment with Solvents

Plant material	Solvent	Treatment time (hours)	Without distillation in steam						With distillation in steam						
			1	2	3	4	5	6	1	2	3	4	5	6	
Corn cob stalks (unnamed varieties)	No pretreatment	—	588	3.57	580	4.23	570	1.49	560	1.21	578	0.54	590	0.36	11.4
	Carbon tetrachloride	48	575	8.43	560	6.77	588	1.88	590	0.46	560	0.14	580	—	17.68
Vaseline oil	No pretreatment	—	48	590	6.85	574	7.98	574	0.70	600	0.33	575	0.10	45.96	6.28
	The same	0.5	580	6.21	580	7.39	560	0.82	592	0.33	560	0.11	570	—	31.40
Sunflower husks	No pretreatment	—	48	580	3.87	574	2.55	569	1.43	570	0.94	570	0.75	575	0.41
	Carbon tetrachloride	48	570	2.89	582	3.68	580	1.79	573	1.32	580	0.65	580	0.36	10.69
Millet husks	Vaseline oil	0.5	575	2.56	590	3.52	575	1.12	580	0.86	569	0.54	569	—	3.74
	The same	—	580	1.36	565	1.43	573	1.29	575	0.73	590	0.66	575	0.41	9.60
Diesel fuel	No pretreatment	—	48	588	2.89	569	4.54	569	1.13	580	0.56	568	0.32	580	0.28
	Carbon tetrachloride	48	570	2.60	572	3.64	580	1.85	568	0.51	570	0.27	575	0.20	9.07
Dichloroethane	Vaseline oil	0.5	575	2.46	573	3.82	575	1.09	573	0.55	588	0.31	580	—	3.49
	The same	0.5	580	2.85	580	3.74	569	1.43	590	0.49	580	0.29	570	—	8.80
Solar oil	Diesel fuel	0.5	590	2.70	590	4.99	568	1.08	590	0.49	575	0.31	572	0.27	2.92
	Dichloroethane	0.5	580	2.39	568	3.6	575	1.20	585	0.56	569	0.20	580	—	3.96
	Solar oil	0.5	580	—	—	—	—	—	—	—	—	—	—	—	35.2

TABLE 2 (Continued)

Plant material	Solvent	Treatment time (hours)	With distillation in steam						Yield increase (%) on raw furfural								
			1	2	3	4	5	6									
Corn cob stalks (unnamed varieties)	No pretreatment	—	1560	4.48	1510	6.31	1518	3.73	1570	0.30	1505	—	—	—	14.82	—	
	Carbon tetrachloride	0.5	1520	9.02	1543	6.91	1511	2.22	1600	0.20	1600	—	—	—	19.35	3.53	23.80
	Dichloroethane	0.5	1500	9.38	1540	7.09	1500	1.64	1550	0.15	1610	—	—	—	18.26	3.44	23.20
	Vaseline oil	0.5	1480	8.14	1510	7.83	1490	1.45	1500	—	—	—	—	—	17.42	2.69	17.50
	Solar oil	0.5	1600	7.82	1508	7.94	1501	1.79	1607	0.02	—	—	—	—	17.57	2.75	18.50
	No pretreatment	—	1500	2.91	1409	3.46	1510	1.85	1550	0.67	1500	—	—	—	8.89	—	—
	Carbon tetrachloride	0.5	1564	6.32	1523	4.76	1525	0.90	1510	—	—	—	—	—	11.98	3.09	34.80
	Dichloroethane	0.5	1523	6.00	1540	5.00	1543	0.57	1510	—	—	—	—	—	11.57	2.68	30.10
	Vaseline oil	0.5	1500	4.98	1510	5.69	1500	0.75	1500	—	—	—	—	—	11.42	2.53	28.40
	Solar oil	0.5	1560	4.09	1520	5.83	1500	1.28	1500	0.26	—	—	—	—	11.46	2.57	28.90

• Calculated on air-dry material.

Under these conditions the furfural yield also increases both during the first and during the second hour of distillation, because of lower losses due to resin formation [2].

Low-boiling solvents were recovered by distillation (86-90%) or by extraction of the residue (78-80%). Pretreatment of large amounts of the hydrolysis material with the above-named organic liquids increases the furfural yield during the first hours of hydrolysis, and may be of practical value as a possible means for intensification of existing processes for furfural production.

This pretreatment results in a higher concentration of furfural in the distillate during the first hours of hydrolysis, and speedier removal of furfural from the reaction medium, so that resinification is diminished. Incorporation of solvent molecules between the furfural molecules in the reaction mass prevents resinification and tends to increase the yields of furfural from different kinds of materials, even those poor in pentosans.

SUMMARY

1. The general course of furfural formation (under analytical conditions, by hydrolysis with 12% hydrochloric acid) is the same for all the samples of raw material studied (sunflower, buckwheat, and millet husks, corn cob stalks, barley husks, oat chaff, rape wastes, tomato and potato haulms, orache stems, and pinewood sawdust). However, the pentosan content in a raw material is not always proportional to the furfural yield from it in a given time; this shows that the pentosans contained in different vegetable materials are not equally easily hydrolyzed.

2. Pretreatment of vegetable raw materials with organic solvents — alcohol, ether, chloroform, carbon tetrachloride, or vaseline oil — results in some leveling of the hydrolysis rate of pentosans by 12% hydrochloric acid, with a more uniform concentration of furfural in the reaction mass and the distillate vapors, leading to an increase of the furfural yield.

Treatment with ligroine or benzene decreases the total yields of furfural from sunflower and buckwheat husks and has almost no effect on the yield from millet husks.

Pretreatment of large amounts of raw materials with such cheap and easily-recovered solvents as dichloroethane, carbon tetrachloride, Diesel fuel, and vaseline and solar oils, prior to hydrolysis by means of 10% sulfuric acid under atmospheric pressure increases the furfural yields (without use of steam) on the average by 2.9% on the raw material or 43.4% calculated on the furfural obtained without the use of solvents. The corresponding values with the use of live steam are 2.9 and 25.7%. The increase in the furfural yield is due to the increase of its concentration in the distillate vapors because of lower resinification during the first hours of hydrolysis.

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THE EFFECTS OF PHENYL- β -NAPHTHYLAMINE AND SULFUR ON OXIDATION OF HYDROCARBONS

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We showed earlier [1, 2] that oxidation of low-molecular hydrocarbons and of vulcanizates swollen in them is a complex interlinked process.

The oxidation rate of swollen vulcanizates and the structural changes taking place in the rubber macromolecules in the process depend on the chemical nature of the solvents and the influence on these processes of various ingredients which act as inhibitors: phenyl- β -naphthylamine, sulfur, accelerators, and the products formed by the decomposition of the latter [3-5].

For a deeper insight into the oxidation mechanism of swollen vulcanizates it was desired to study the effects of phenyl- β -naphthylamine and sulfur on the oxidation of low-molecular hydrocarbons of different chemical types. These ingredients were selected because they are constituents of nearly all vulcanized rubbers, and also because their inhibiting effects in the oxidation of rubber have been studied in greatest detail.

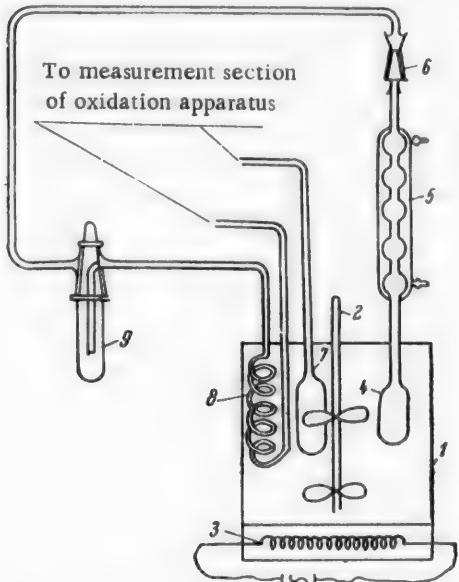


Fig. 1. Diagram of apparatus for oxidation of swollen vulcanizates: 1) thermostat, 2) stirrer, 3) electric heater, 4) bulb, 5) condenser, 6) ground-glass joint, 7) barostatic vessel, 8) coil, 9) trap.

Accordingly, the oxidation of the following systems was studied: 1) solvents* in presence of phenyl- β -naphthylamine; 2) solvents* in presence of phenyl- β -naphthylamine and sulfur; 3) swollen vulcanizates.

This investigation has a direct bearing on the aging of rubbers in contact with low-molecular hydrocarbons. In such cases the free ingredients may be dissolved out of the rubber by the hydrocarbons and influence the inter-linked oxidation of the rubber and the swelling agent.

The solvents used were individual hydrocarbons (tetralin and decalin), which differ in their reactivity to oxidation by molecular oxygen. The oxidation kinetics of the solvents and of the swollen vulcanizates were studied with the aid of an oxidation unit which differed substantially from the apparatus used for oxidation of rubber [6]. The modifications introduced into the apparatus described earlier are shown in Fig. 1. In this case, the reaction vessel was the bulb 4, with a reflux condenser for the solvent vapors sealed to it. To prevent entry of uncondensed solvent vapor into the gas buret, the apparatus included the separable trap 9, cooled in a mixture of solid carbon dioxide and acetone during the experiments.

Because of the high viscosity of the degraded vulcanizates in the swollen state, oxidation of the swollen

* The term "solvents" is used here to describe the various hydrocarbons of low molecular weight used as swelling agents.

vulcanizates and of the solvents was effected without stirring. The volume of solvent was 1.5 ml and the weight of vulcanize was 0.2 g* in all the experiments, so that any possible diffusion effects would influence hydrocarbon oxidation equally.

Oxidation of Solvents in Presence of Phenyl- β -Naphthylamine

Phenyl- β -naphthylamine has different effects on the oxidation of tetralin and decalin, respectively. Figures 2 and 3 (Curves 2) contain kinetic curves for the oxidation of the solvents by molecular oxygen in presence of the amine. It is seen that phenyl- β -naphthylamine has little influence on the oxidation kinetics of tetralin, but retards the oxidation of decalin appreciably.

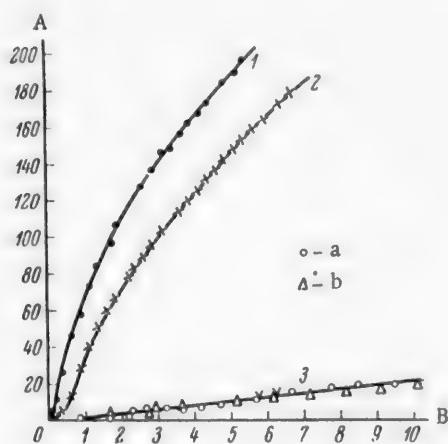


Fig. 2. Effect of inhibitors on the oxidation of tetralin at 150°. A) Amount of O_2 (millimoles/mole), B) time (hours); solvents: 1) tetralin, 2) tetralin and phenyl- β -naphthylamine (0.15 wt. %), 3a) tetralin, phenyl- β -naphthylamine (0.15 wt. %), and sulfur (0.3 wt. %), 3b) tetralin and sulfur (0.006 wt. %).

It is known that oxidation of hydrocarbons at moderate temperatures (about 100–150°) is accompanied by accumulation of peroxides. It was accordingly necessary to study the effect of the amine on the accumulation kinetics of peroxides in the solvents. It is clear

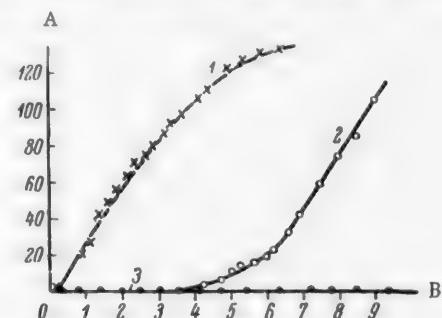


Fig. 3. Effect of inhibitors on the oxidation of decalin at 150°. A) Amount of O_2 (millimoles/mole), B) time (hours); solvents: 1) decalin, 2) decalin and phenyl- β -naphthylamine (0.15 wt. %), 3) decalin and phenyl- β -naphthylamine (0.15 wt. %), and sulfur (0.3 wt. %).

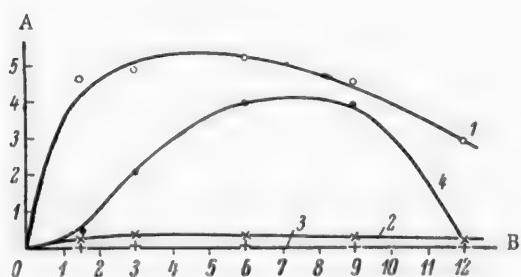


Fig. 4. Kinetics of peroxide accumulation in the oxidation of tetralin in air. A) Peroxide content (mg active O_2 /g of solvent); B) time (hours); oxidation temperature ($^{\circ}$ C): tetralin, 1) 120, 2) 150, 3) 180, tetralin with phenyl- β -naphthylamine (0.15 wt. %), 4) 120.

from Figs. 4 and 5 that phenyl- β -naphthylamine has relatively little effect on the course of accumulation of tetralin peroxides at 120°. In the oxidation of decalin in presence of phenyl- β -naphthylamine at the same temperature no peroxides were detected. On increase of the reaction temperature to 150° the oxidation reaction is retarded during the first six hours. On further oxidation of decalin considerable amounts of peroxides accumulate, although the concentration of peroxides formed in the oxidation of the hydrocarbon in absence of the inhibitor is 1.6 times the maximum concentration in its presence.

The amine is expended during oxidation of the solvents. As Fig. 6 shows, when tetralin is oxidized in air at 150° the consumption of the inhibitor is slight. In the oxidation of decalin, the amine is expended almost completely during the first six hours of oxidation, and

* Finely-shredded vulcanizates were used in the experiments.

the rate of peroxide accumulation is not high (Fig. 3). Intensive accumulation of peroxides begins only by the time the phenyl- β -naphthylamine has been expended almost completely.

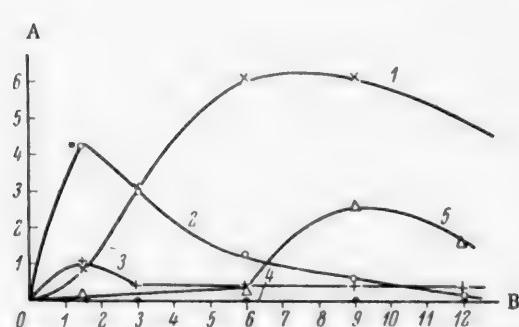


Fig. 5. Kinetics of peroxide accumulation in the oxidation of decalin in air. A) Peroxide content (mg active O_2 /g of solvent); B) time (hours); oxidation temperature ($^{\circ}C$): decalin, 1) 120, 2) 150, 3) 180, decalin with phenyl- β -naphthylamine (0.15 wt. %), 4) 120, 5) 150.

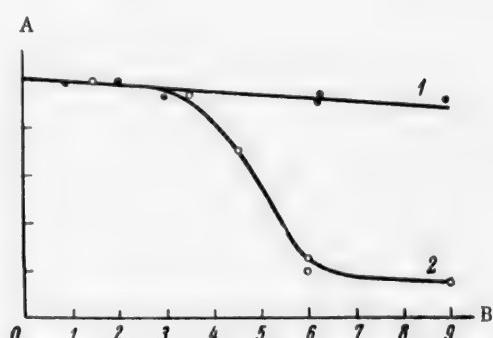


Fig. 6. Consumption of phenyl- β -naphthylamine in the oxidation of hydrocarbons in air at 150°. A) Content of phenyl- β -naphthylamine (%), B) time (hours); curves: 1) tetralin, 2) decalin.

It is now generally accepted that relatively stable peroxides play the decisive role in the development of autocatalytic oxidation of hydrocarbons [7]. It was therefore of interest to study the decomposition of tetralin and decalin hydroperoxides* under vacuum, in presence of phenyl- β -naphthylamine. The results are plotted in Figs. 7 and 8. It follows from these results that phenyl- β -naphthylamine has no significant influence on the thermal decomposition of tetralin and decalin peroxides. It follows that phenyl- β -naphthylamine does not interact with tetralin or decalin hydroperoxides. The great difference between the behavior of the inhibitor in the oxidation of decalin and tetralin, respectively, can be explained on the assumption that the peroxide radical of

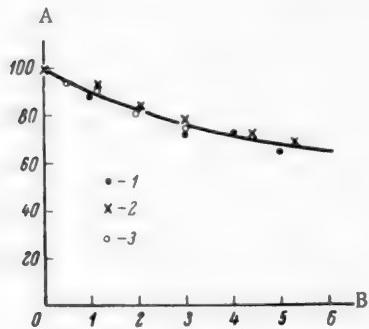


Fig. 7. Effect of inhibitors on the decomposition of tetralin hydroperoxide at 120°. A) Peroxide content (%); B) heating time (hours); curves: 1) tetralin, 2) tetralin and phenyl- β -naphthylamine (0.15 wt. %), 3) tetralin, phenyl- β -naphthylamine (0.15 wt. %), and sulfur (0.3 wt. %).

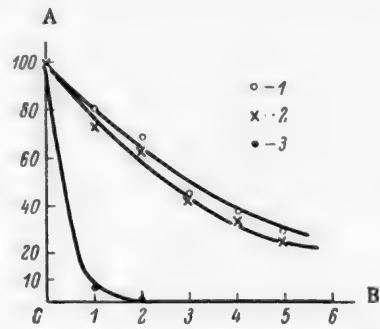


Fig. 8. Effect of inhibitors on the decomposition of decalin hydroperoxide at 150°. A) Peroxide content (%); B) heating time (hours); curves: 1) decalin, 2) decalin and phenyl- β -naphthylamine (0.15 wt. %), 3) decalin, phenyl- β -naphthylamine (0.15 wt. %), and sulfur (0.3 wt. %).

* For determination of the decomposition kinetics of their peroxides, decalin and tetralin were previously oxidized in air at 120° for 5 and 3 hours, respectively.

decalin can detach a hydrogen atom more easily from phenyl- β -naphthylamine than from the original hydrocarbon, with formation of a hydroperoxide and an unreactive amine radical. The peroxide radical can react more easily with the inhibitor molecule (AH) than with the original hydrocarbon (RH) if the A-H bond is weaker than the R-H bond. The hydrogen atoms in the α -methylene groups of the hydrogenated ring in the tetralin molecule are incomparably more mobile than the hydrogen atoms in the decalin molecule [8]. Therefore, it is probable that the tetralin peroxide radicals are more easily stabilized by removal of hydrogen from the original hydrocarbon than from the amine. As a result, despite the presence of phenyl- β -naphthylamine, which does not interact with the stable tetralin peroxides, the chain length and the oxidation rate of tetralin change little.

The fact that when decalin is oxidized in presence of phenyl- β -naphthylamine the solution acquires a bright orange color suggests that when oxygen reacts with the amine radical a compound with a quinoid structure is formed.

It is known [9] that at temperatures of about 180° a more important role should be played by aldehydes, formed mainly by decomposition of the peroxide radicals. This raises the question of the interaction of the amine with aldehydes formed by oxidation of hydrocarbons. Unfortunately, the literature contains no information on this question.

Oxidation of Solvents in Presence of Phenyl- β -Naphthylamine and Sulfur

Sulfur* has a more pronounced influence than phenyl- β -naphthylamine on the oxidation kinetics of the solvents. The combined effect of sulfur and phenyl- β -naphthylamine on the kinetics of hydrocarbon oxidation differs little from the effect of sulfur alone (Fig. 2). The effects of sulfur on the oxidation of different solvents are different. As Fig. 3 shows, when decalin is oxidized in presence of sulfur and phenyl- β -naphthylamine there is apparently no absorption of oxygen at all. Oxidation of tetralin in presence of the same additives develops at a constant but rather low rate (Fig. 2). The oxidation of the two solvents in presence of sulfur is virtually unaccompanied by peroxide formation. The rate of thermal decomposition of tetralin hydroperoxides at 120° in

presence of sulfur and phenyl- β -naphthylamine does not differ from their decomposition rate in absence of sulfur (Fig. 7). Quite different results are obtained in the thermal decomposition of decalin hydroperoxides in presence of the same additives. In this case the peroxides are almost completely decomposed at 150° in 1 hour (Fig. 8).

The observed acceleration of the decomposition of decalin hydroperoxides (ROOH) in presence of sulfur is possibly due to the fact that the sulfide radicals formed by the reactions of sulfur with RO[•] and 'OH radicals are sufficiently active for development of a chain reaction of hydroperoxide decomposition. Acceleration of the decomposition of isopropylphenyltriazene in presence of sulfur has been reported earlier [10].

Our observations concerning the consumption of phenyl- β -naphthylamine during oxidation in the system solvent—phenyl- β -naphthylamine—sulfur are worthy of note. In this case, the situation with regard to the consumption of phenyl- β -naphthylamine is the reverse of that seen in oxidation in the system solvent—phenyl- β -naphthylamine. It follows from Fig. 9 that oxidation of

Fig. 9. Consumption of phenyl- β -naphthylamine in the oxidation of hydrocarbons in air. A) Content of phenyl- β -naphthylamine (%); B) time (hours); curves: 1) tetralin with sulfur (0.3 wt. %), 2) decalin with sulfur (0.3 wt. %).

tetralin in presence of sulfur is accompanied by consumption of the amine, whereas the amine is not consumed in the oxidation of decalin. Sulfur appears to paralyze the effect of the amine in the oxidation of decalin. A similar effect was observed in oxidation in the system rubber—phenyl- β -naphthylamine—sulfur [11]. It is still unknown why sulfur paralyzes the action of phenyl- β -naphthylamine in the oxidation of some hydrocarbons but not others. It should be noted that if the amine is consumed the solution acquires a bright orange color in course of oxidation.

* The sulfur, recrystallized from benzene, melted at 116.5°.

Oxidation of Swollen Vulcanizate

Curves for the oxidation kinetics of vulcanizates swollen in decalin and tetralin are given in one of our earlier papers [1]. It may be noted here that in the course of oxidation of vulcanizate—solvent systems no stable peroxides were detected in the 120–180° range. The data in the table indicate that acids are formed during oxidation of swollen vulcanizates.

Accumulation of Acids During Oxidation in the System
Vulcanizate—Solvent in Air

Time from start of expt. (hours)	Acid No. for system vul- canizate—decalin at temp. (in °C)			Acid No. for system vul- canizate—tetralin at temp. (in °C)		
	120	150	180	120	150	180
1 1/2	0.29	0.335	0.363	0.279	0.031	0.920
3	0.363	0.826	0.436	0.334	0.822	0.975
6	0.69	0.835	0.363	0.419	0.836	0.836
9	0.799	—	0.436	0.362	0.906	0.999
12	0.908	0.799	0.363	0.447	0.878	1.129

It follows from the data in the table that the amount of acids formed during oxidation in the system vulcanizate—solvent at 120, 150, and 180° is relatively small. The acid number increases somewhat with increase of temperature from 120 to 150°; this is more appreciable for vulcanizates swollen in tetralin. On increase of temperature from 150 to 180° the acid number is either almost unchanged or decreases. The latter is found for the system vulcanizate—decalin.

SUMMARY

1. The influence of phenyl-β-naphthylamine on oxidation of decalin and tetralin was studied; it was found that the amine has relatively little effect on the oxidation of tetralin, and retards the oxidation of decalin very considerably.
2. The difference between the effects of phenyl-β-naphthylamine on the oxidation of these two hydrocarbons is due to stabilization of the decalin peroxide radical by removal of hydrogen atoms from amine molecules with formation of inactive radicals which are incapable of continuing the reaction chain. In the oxidation of tetralin this reaction is much less pronounced, as tetralin peroxide radicals can detach hydrogen more easily from molecules of the original hydrocarbon than from the amine.
3. Phenyl-β-naphthylamine does not react with the stable hydroperoxides of tetralin and decalin.
4. Sulfur in conjunction with phenyl-β-naphthylamine has a stronger inhibiting effect in the oxidation of decalin than in the oxidation of tetralin. The difference in the behavior of the inhibitors in these systems is due to reactions of sulfur with the radicals formed in the decomposition of stable decalin peroxides.

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A MMONOLYSIS OF BENZALDEHYDE OVER MIXED OXIDE CATALYSTS

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Reactions of oxygen-containing aromatic compounds with ammonia, resulting in the formation of amines and nitriles, have attracted increasing attention of research workers in recent years [1]. The vapor-phase ammonolysis of benzaldehyde is a reaction of considerable interest, as this method yields a valuable organic intermediate, benzonitrile, without the use of highly toxic cyanides.

Ammonolysis of aliphatic and aromatic aldehydes, including benzaldehyde, proceeds best over copper, nickel, cobalt, and copper-cobalt catalysts. The aldehydes and ammonia are fed into the reaction vessel in ratios of 1:1 to 1:10. The optimum reaction temperature is in the 275-500° range. Under these conditions up to 45-50% benzonitrile can be obtained from benzaldehyde [2-4].

Many nitriles can be obtained over oxide catalysts commonly used for vapor-phase oxidation of organic compounds [5, 6]. For example, Mowry [7] reported that benzaldehyde undergoes 30-40% conversion into benzonitrile over thorium oxide at 420-440°.

The purpose of the present investigation was to study ammonolysis of benzaldehyde over mixed oxide catalysts—titanium vanadate and tin vanadate.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The reaction was carried out in an all-metal reactor with a stainless steel reaction tube, 21 mm in diameter and 1100 mm long, heated in an electric furnace. Benzaldehyde was fed from an apparatus the design of which was described earlier [8]. Ammonia entered the reactor from a cylinder, the flow rate being measured by a rheometer. The reaction products were collected in a two-liter flask cooled in ice and connected to a reflux condenser.

Freshly distilled benzaldehyde with b. p. 176-176.5° (690 mm), d_{4}^{20} 1.048, n_{D}^{20} 1.5462 was used for each experiment. The benzoic acid content generally did not exceed 2%.

The titanium vanadate and tin vanadate catalysts were measured by the methods of Pongratz [9] and Rubinshtein [10], and were granulated into grains 3-5 mm in diameter before being charged into the reactor.

Benzaldehyde was fed into the reaction chamber at a rate of 130 g per liter of catalyst per hour, and ammonia was supplied in 5-fold excess over the theoretical quantity. The contact time was 6 seconds in all the experiments. At the end of each experiment the contents of the collecting system were transferred to a separating funnel, and the oily layer was separated from the aqueous. It was washed with 1% potassium permanganate solution, sodium carbonate, and distilled water, and dried over calcined sodium sulfate. Distillation of the product usually yielded two fractions:

- I 105-113° (690 mm Hg), n_{D}^{20} from 1.4957 to 1.4968,
- II 186-188° (690 mm Hg), n_{D}^{20} from 1.5277 to 1.5288,
- III Nonvolatile residue.

Fraction I corresponded to toluene by its boiling point and refractive index. Oxidation of this fraction by 5% potassium permanganate solution gave benzoic acid in 65% yield; it melted at 122-123° and had neutralization equivalent 122.7. Fraction II was benzonitrile. When boiled with 50% sulfuric acid at 100-110° for 2 hours it gave benzoic acid in approximately 80% yield. This melted at 122.5° and had the theoretical neutralization equivalent. The benzonitrile fraction was redistilled and analyzed for nitrogen, with the following results:

0.00538 g substance: 0.694 ml N₂ (22°, 692 mm Hg);

0.00616 g substance: 0.792 ml N₂ (22°, 689 mm Hg);

Found %: N 13.57, 13.50. C₇H₅N. Calculated %: N 13.59.

The solid residue in the flask melted at 274-275° after recrystallization from boiling ethyl alcohol. Its molecular weight, determined cryoscopically in glacial acetic acid, was 282-295. Elementary analysis gave the following results:

0.00431 g substance: 0.01352 g CO₂, 0.00207 g H₂O;

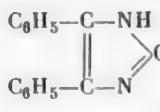
0.00382 g substance: 0.01194 g CO₂, 0.00186 g H₂O;

0.00354 g substance: 0.323 ml N₂ (21°, 693 mm Hg);

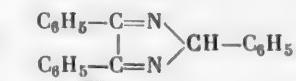
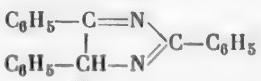
0.00484 g substance: 0.451 ml N₂ (22°, 689 mm Hg).

Found %: C 85.61, 85.30; H 5.38, 5.45; N 9.64, 9.77.

The physicochemical properties of the substance suggested that it was lophine, the structure of which, according to available literature data, is represented by one of the following structural formulas [11]:

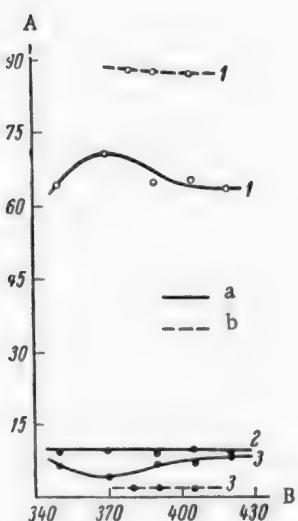


I



II

III



Ammonolysis of benzaldehyde over titanium vanadate catalyst.
A) Yield of reaction products (%); B) reaction temperature (in °C). 1) Benzonitrile, 2) lophine, 3) toluene; a) experiments with liquid benzaldehyde, b) experiments with benzaldehyde vapor.

To prove that our product was identical with lophine, the latter was synthesized by dry distillation of hydrobenzamide, which was prepared from a mixture of benzaldehyde and concentrated aqueous ammonia, left to stand for many days. The synthesized lophine had m. p. 274°, after recrystallization from alcohol. A mixed sample with the product formed by ammonolysis of benzaldehyde melted at the same temperature. Both substances gave white crystals, melting at 115°, with hydrochloric acid. A mixed sample gave no depression.

The results of experiments on the reaction of benzaldehyde with ammonia over titanium vanadate catalyst are shown in the graph. It is seen that the main reaction product is benzonitrile, the yield of which varies with the temperature and reaches a maximum at 370-380°. Very little toluene is obtained, but its yield increases somewhat with temperature. The yield of lophine remains almost constant over the entire temperature range studied.

Analogous results were obtained in ammonolysis of benzaldehyde over tin vanadate catalyst. The main reaction product was again benzonitrile, the yield of which reached 73% of the theoretical. In addition to benzonitrile, the reaction products contained toluene and lophine in yields similar to those in experiments with titanium vanadate.

It must be pointed out that in all these experiments part of the lophine formed remained in the reaction tube. To extract it, superheated steam was blown through the reaction tube after each experiment. This fact, and also the constancy of the lophine yield at different temperatures, suggested that lophine is not a product of vapor-phase catalytic ammonolysis

of benzaldehyde, but is formed in the upper and cooler part of the reactor by the action of ammonia on liquid benzaldehyde, not yet vaporized, entering from the metering device. This reaction should proceed through the intermediate stage of hydrobenzamide formation.

To prevent contact between liquid benzaldehyde and ammonia the feed system was modified somewhat. Before entering the reactor, benzaldehyde passed through an evaporator heated to 270°, and mixed in vapor form with ammonia in the reactor. The upper part of the reactor was also heated to the same temperature. Experiments performed under these conditions confirmed our hypothesis. The results, shown in the same diagram, indicate that only traces of lophine were formed in this case, while the benzonitrile yield rose to 87-88%.

SUMMARY

1. When benzaldehyde and ammonia react in presence of titanium vanadate or tin vanadate, the main direction of the process is formation of benzonitrile, which is obtained in 87-88% yield over a wide temperature range.

2. The lophine present in small amounts among the ammonolysis products of benzaldehyde is formed in a parallel side reaction. Another side reaction, also of small extent, is hydrogenation of benzaldehyde to toluene, probably by the hydrogen liberated in the ammonolysis of the original substance:



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METHODS FOR SIMPLIFICATION OF HIGH-MOLECULAR SUBSTANCES IN PITCH*

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In the existing process for conversion of wood tar, pitch is invariably formed in 30-70% yield. Until recently pitch has been almost a burdensome waste product. The existing outlets for pitch (for waterproofing materials, as plastifier for mortars and concretes, and principally for "DP" foundry core binder production) will not be able to absorb all the pitch produced if the volume of tar conversion increased, and therefore it is already necessary to seek new uses. Rational search can be possible only after the qualitative and quantitative composition of wood pitch has been determined, at least approximately.

Literature data on the subject are very scanty. The views of some authors [1, 2] are purely conjectural, unsupported by even the simplest analytical data, while others [3] give only general physicochemical characteristics. The first data on the group composition of pitch were obtained by Marcusson and Picard [4]. They separated pitch from beechwood dry-distillation tar into hydroxy acids, neutral substances, phenols, and fatty acids. Bobrov and others [5] performed similar separation of Ashinsk and Vetluga pitch. This is all the information available in the literature on the chemical composition of wood pitch. It is seen from the foregoing that it deals only with the properties of principal groups of compounds. Nothing is known about the chemical nature of the latter.

The purpose of the present investigation was to determine the chemical nature of individual pitch components.

Gas-producer pitch was used in the experiments. First, a small sample of pitch was separated by our method, as an exploratory experiment. The pitch was obtained from freshly collected tar from the gas producer in one of the factories, in 27% yield calculated on the bone-dry tar. The softening temperature of the pitch was 69°, acid number 137, saponification number 157. The sample contained 24.8% neutral substances, 21.4% phenols, and 42.7% acids. The primary characteristics of these groups were determined. It was found that the first two groups were of relatively low molecular weight, and could be distilled under 0.05-0.15 mm residual pressure. The acids were undoubtedly of high molecular weight.

These preliminary experiments were followed by separation of a large sample of gas-producer pitch from the Vetluga works, with softening temperature 90° and saponification number 130. This sample contained 65.5% "phenols" (it was later found that they were phenolic acids) and 5.8% acids.

The groups of compounds isolated from the pitch were investigated, main attention being devoted to study of water-insoluble phenols (phenolic acids), the principal components of pitch.

The phenolic acids are products of high molecular weight, and therefore in order to obtain information on their chemical structure it is necessary to find one or more methods for splitting their large molecules into substances of low molecular weight, the structure of which would give an indication of the structure of the original phenolic acids. Among the methods tested for simplification of the phenolic acid molecules were distillation with zinc dust, dry distillation, alkaline hydrolysis, splitting by metallic sodium by Shorygin's method, and oxidation by nitrobenzene by Freudenberg's method.

* Communication 1 in the series on studies of the chemical composition of pitch from gas-producer wood tar.

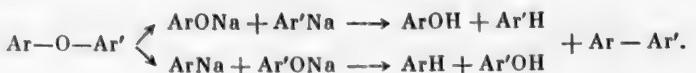
Distillation with zinc dust proved to be quite useless, as the yield of low-molecular products was negligible.

The yield of low-molecular products in dry distillation was also low, only 15%. The densities and refractive indices of individual neutral fractions indicated that the latter were of the aromatic series. All the characteristics of the first phenolic fraction correspond to ordinary creosote phenols and the fraction contains about 20% guaiacol. The formation of aromatic neutral substances and phenols indicates that the structural units in the phenolic acids are aromatic in character.

The oxygen balance was calculated from the general characteristics of the phenolic acids. A difference (13.7%) was found between the oxygen content of the functional groups. In view of the absence of lactone and carbonyl groups, the difference may be attributed either to ether linkages or to heterocyclic compounds with oxygen in the ring.

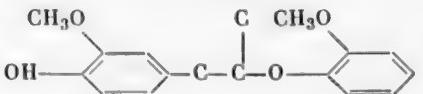
The ether-bond hypothesis led to the use of alkaline hydrolysis [6] to break down the phenolic acids. The experimental results show that fairly extensive simplification of phenolic acids is effected by alkaline hydrolysis. Whereas the original phenolic acids were completely insoluble in ether, hydrolysis yielded about 60% of ether-soluble substances, consisting mainly of substances of phenolic character mostly of molecular weight up to 300. It follows that a large number of structural units in phenolic acids are linked by ether bonds.

The mildest method for simplification of high-molecular substances of this type is by the action of metallic sodium dissolved in liquid ammonia, by Shorygin's method [7]. The ether bonds are split relatively easily according to the scheme:



After threefold treatment of the phenolic acids, 34% of ether-soluble substances with molecular weights from 300 to 500, and 60% of substances soluble in alcohol-acetone mixture, with molecular weight about 800, were obtained. Although this method does yield simplification products of a low degree of degradation, the procedure is difficult and not very suitable because sufficient amounts of the products for investigation cannot be obtained.

Finally, the last simplification method to be tried was oxidative decomposition by nitrobenzene, by Freudenberg's method [8]. The basis for this type of oxidation was provided by Leopold's report [9] on the oxidation of model substances containing ether linkages between benzene rings, of the type



In different experiments on oxidative decomposition by nitrobenzene we obtained from 19 to 27% of ether-soluble products with molecular weights up to 300.

Comparison of various methods for simplification of complex phenolic acid molecules shows that alkaline hydrolysis is the most suitable because of its ease and the considerable yields of low-molecular products.

EXPERIMENTAL

Methods for separating pitch into principal groups of compounds: 1) Saponification by 5% aqueous alkali for 3 hours on a boiling water bath; 2) separation of the insoluble portion on an asbestos filter; 3) ether extraction of neutral substances; 4) separation of water-insoluble phenols precipitated on saturation of the solution with carbon dioxide; 5) ether extraction of water-soluble phenols; 6) separation of water-insoluble acids precipitated on acidification of the solution with hydrochloric acid; 7) evaporation of the filtrate to dryness, and isolation of volatile acids from the distillate; 8) acetone extraction of the organic portion from the dry residue.

Separation balance (%)

Impurities insoluble in alkali	5.7
Neutral substances	12.5
Water-insoluble phenols	65.5
Water-soluble phenols	3.5
Water-insoluble acids	5.8
Acids volatile in steam	0.2
Organic portion of dry residue	3.2
Losses	3.6

General characteristics of the phenolic acids. The phenolic acids form an infusible powder, insoluble in ether, alcohol, acetone, ligroine, benzene, acetic acid, amyl acetate; soluble in phenol, acetic anhydride, and pyridine.

Elementary composition (%): C 64.25; H 6.35; O 29.40. Methoxyl content 3.55%. Acid number, determined by potentiometric titration and by titration in presence of phenolphthalein, was 99, the equivalent was 566. Acetyl number 302, equivalent 195; saponification number 99. Hydrazone was not formed (nitrogen was not determined by Dumas and Kjeldahl methods).

Thus, the oxygen contents of the functional groups were:

$$\begin{aligned}
 &\text{in } \text{OCH}_3 \frac{16}{31} \cdot 3.55 = 1.85\% \\
 &\text{in } \text{COOH} \frac{32}{566} \cdot 100 = 5.65\% \\
 &\text{in } \text{OH} \frac{16}{195} \cdot 100 = 8.20\% \\
 \hline
 &\text{Total} \quad 15.7\% \\
 &\text{Difference} \quad 29.4 - 15.7 = 13.7\%
 \end{aligned}$$

Dry distillation. Dry distillation to a final temperature of 405° inside the retort for 12 hours yielded 58% of carbon, and 30.7% of an aqueous distillate. The aqueous distillate contained 0.6% acids calculated as phenolic acids, 11.0% neutral substances, and 3.45% phenols.

The equivalent of the acids was 85.

The phenols were fractionated at 10 mm residual pressure:

$$\begin{aligned}
 1 \text{ fraction } 80-100^\circ &- 44\% \\
 2 \text{ fraction } 100-152^\circ &- 17.4\%
 \end{aligned}$$

Fraction 1: $n^{20}\text{D}$ 1.545; d^{15}_4 1.066; contents (%): OH 14.6, OCH_3 5.3.

The neutral substances had the following fractional composition at 7 mm:

	Yield in %	$n^{20}\text{D}$	d^{15}_4	% OH
1 fraction to 115°	21.8	1.521	0.954	0.0
2 fraction 115-175°	26.3	1.576	1.014	0.0
3 fraction 175-190°	13.2	—	—	0.0
Residue	38.7	—	—	—

Alkaline hydrolysis. Hydrolysis by means of 16.6% caustic soda solution was performed in an autoclave at 285° for 3 hours at 1:1 ratio of alkali to phenolic acids.

Typical saponification balance

Carbon dioxide (%)	4.5
Water - insoluble (%):		
extracted in ether	44.0
insoluble in ether	24.0
Water - soluble (%):		
extracted in ether	10.0
acids from aqueous distillate	2.8
organic portion of dry residue	2.1
Losses (%)	12.5%

The substances extracted in ether from the water-insoluble fraction form a thick paste, 40% of which can be distilled at 40°C - 220°C . The distillate contains 85% phenols of the following fractional composition:

	Boiling point at 0.25 mm Hg	Yield, (in %)
1 fraction	to 95°	5.2
2 fraction	95-145°	12.2
3 fraction	145-180°	29.5
4 fraction	180-190°	22.5
Residue	-	30

Combined fractions 3 and 4 crystallized after prolonged standing; they had molecular weight 300 and the composition: C 78.1%; H 10.1% and O 11.8%. The approximate (doubled) formula is $\text{C}_{18}\text{H}_{28}\text{O}_2$.

Decomposition by metallic sodium in liquid ammonia. After 3 treatments (5 days each) of the phenolic acids at room temperature in a glass beaker placed in an autoclave with phenolic acids, sodium, and ammonia in 1:1:8 ratio, the following yields were obtained (%):

ether-soluble substances	34.1
including		
neutral substances	5.9
acids	5.0
phenols	23.2
Soluble in alcohol-acetone mixture	60.0

Molecular weight by the Rast method: phenols 300, acids 500, alcohol fraction 800.

Oxidative decomposition by nitrobenzene. When 20 g of phenolic acids was heated in 800 ml of 2 N NaOH solution with 80 ml of nitrobenzene for 4 hours at 160-170° in an autoclave, from 7.7 to 9.4% acids, and from 9.4 to 19.0% phenols of molecular weight not above 300 was obtained.

SUMMARY

In development of methods for simplification of high-molecular substances in pitch it was found that the fundamental structural units in phenolic acids are linked by carbon-carbon bonds into substances of relatively low molecular weights, from 300 to 800. These are joined into high molecular phenolic acids by means of ether linkages formed from hydroxyls of different molecules by polycondensation.

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ALKALINE HYDROLYSIS OF SCHOLLER'S LIGNIN WITH FORMATION OF SUBSTANCES OF LOW MOLECULAR WEIGHT

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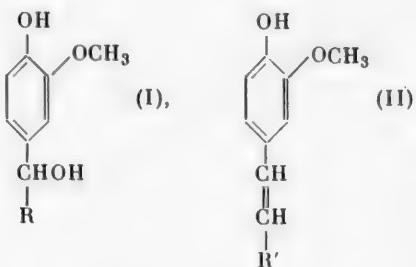
The problem of efficient utilization of technical lignins (hydrolytic, sulfate process, lignosulfonates) has not yet been solved, despite numerous investigations, and they largely remain waste products. Combustion of sulfate and hydrolytic lignins, and an approach to a solution of the problem of combustion of evaporated sulfite waste liquors, makes it possible to utilize at least their calorific value and to get rid of harmful wastes. Utilization of these lignins without preliminary extensive chemical processing (addition to phenolic resins and use as active filler for rubber etc., in the case of sulfate lignin; use of lignosulfonates as core binders, tanning agents, additives to clinker, etc.), is possible and feasible. However, such uses cannot absorb the enormous amounts of waste lignin (over 1,000,000 tons per year in our country). Therefore, in the USSR and all over the world sulfite waste liquors, for example, are discharged as effluents.

Deep chemical conversion of these lignins has not yet yielded significant results. Vanillin may be obtained from them by alkaline oxidation but only very limited amounts of lignins can be utilized in this way.

It is generally accepted that lignins of conifers and deciduous trees are built up from hydroxymethoxy-phenylpropane units.

The manner in which these units are linked in the lignin macromolecule is not known precisely and therefore there are as yet no generally accepted structural formulas for lignins. The molecular weight of lignins not subjected to chemical action (Bjorkman's lignin, made by extraction of colloidally ground wood with organic solvents) is fairly high, about 11,000 [1]. Oxidation of spruce wood by alkaline nitrobenzene yields 31% aldehydes, (90% of which is vanillin), calculated on the lignin; birchwood yields 47% (75% syringaldehyde).

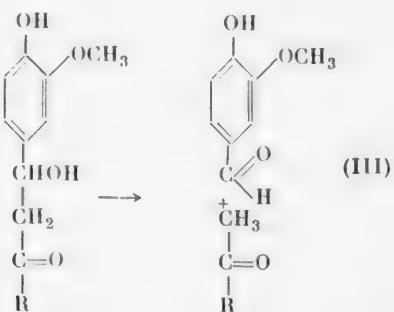
Under these conditions derivatives of 3-methoxy-4-hydroxyphenylpropane give 80-90% of vanillin if they contain a hydroxyl or a double bond at the α -carbon atom (**I**, **II**) [2].



On these grounds Leopold considers that in spruce lignin not subjected to acid treatment 40-50% of the aromatic rings are 3-methoxy-4-hydroxyphenyl groups [3]. Therefore, there should be 0.4-0.5 equivalent of phenolic hydroxyl for each phenylpropane unit. The same values (0.4-0.6 equivalent) were also obtained for the most diverse lignins by potentiometric titration of phenolic hydroxyls by tetramethylammonium hydroxide in ethylenediamine or in dimethylformamide [4]. It follows that lignin macromolecules are not linear but strongly branched with 3-methoxy-4-hydroxyphenyl groups at the branch ends. The fact that the content of

phenolic hydroxyls remains constant irrespective of the method (acid, alkaline, etc.) used to isolate the lignin from wood shows that phenolic hydroxyls are not involved in lignin condensation reactions. We have postulated a condensation mechanism with the participation of α -alcoholic hydroxyls in the phenylpropane structural units and hydrogen atoms from the benzene rings [5], which should lead to formation of carbon-carbon bonds between molecules and decrease of vanillin yields in alkaline oxidation of "condensed" lignins, [6, 7]. According to our views [5] "condensation" should double, treble, etc., the average molecular weight of lignin; since the initial molecular weight of native lignin is fairly high (approximately 10,000), this should not lead to any significant increase of the percentage content of carbon-carbon bonds between phenylpropane units in technical lignins.

It is now assumed that phenylpropane units in the lignin macromolecule are linked both by carbon-carbon and by carbon-oxygen (ether) bonds [8] in approximately equal numbers. The work of Kratzl and his associates [9] has shown that substances of structure (III) undergo a reaction which is the reverse of aldol condensation when heated with aqueous alkali and this accounts for the formation of vanillin (5-7%) when lignosulfonates are heated with alkali:



It follows that some carbon-carbon bonds in lignins are not broken by the action of aqueous alkali at moderate temperatures (not above 160°). Leopold showed that oxidation of low-molecular lignosulfonates (less-condensed lignin) by nitrobenzene and alkali yields up to 40% of vanillin, whereas a technical mixture of lignosulfonates (more-condensed lignin) gives not more than 25% [10], with rupture of carbon-carbon bonds at the ends of type (I) lignin molecules. One of the present authors and co-workers showed earlier that phenol ethers are quantitatively hydrolyzed when heated with aqueous alkali [11]. Hence, it follows that if technical lignins are heated with aqueous alkali in the conditions for alkaline hydrolysis of phenol ethers (1.5-3 hours, 260-280°, caustic soda concentration 5-15%) the ether linkages in the lignin macromolecules should be hydrolyzed and the bonds at the ends of type (III) molecules should be broken. This would convert lignin into a mixture of substances of a phenolic character and of relatively low molecular weight.

Under the reaction conditions these substances would doubtless undergo further conversion. It should be noted that according to our data, guaiacol gives a carbonaceous residue and caproic acid by the action of aqueous alkali above 290°. Therefore, the pyrocatechol formed under these conditions decomposes with disproportionation of hydrogen, giving a product of higher hydrogen content (caproic acid) and one of lower hydrogen content (carbonaceous residue). It is known that cyclohexanol also gives caproic acid by alkaline fusion above 300° [12]. It follows that temperatures above 290° are inadmissible in the heating of lignin with aqueous and fused alkalies for the production of phenols.

When technical lignins are fused with anhydrous alkali, up to 15-20% of pyrocatechol and protocatechuic acid is formed [13]. Because of the low yields of these substances and the high irretrievable consumption of alkali, this process cannot be regarded as technically promising.

Fischer et al. [14] heated Willstätter's lignin with 10 N alkali (400 g/liter) at 300° and obtained 17% of carbon dioxide, 16% of alkali-insoluble residue, 4% of oxalic acid, 40% of "humic acids," about one-half soluble in ether, 8% of volatile acids, 18% of substances insoluble in water or ether and a little hydrogen. They did not investigate these products. As will be shown below, such high alkali concentrations and temperatures are inadvisable.

If the following considerations are valid, when various technical lignins are heated with aqueous alkali under the stated conditions phenolic substances of relatively low molecular weight should be obtained, in yields which depend relatively little on the kind of original lignin. To test this hypothesis we used Scholler's (hydrolytic) lignin, which is insoluble in all reagents and is therefore regarded as the most highly condensed (with the greatest molecular weight). Our views would be confirmed if such alkali treatment yielded a mixture of substances of the type indicated.

Lignin samples 50-90 g in weight, at 11-12 liquor ratio, were subjected to the alkali treatment; the heating time at the indicated temperature was 2 hours; the temperature was 270-275° in the first experiment and 275-285° in the others; in the second experiment a copper insert [11] was put into the autoclave. In the first experiment no gas was obtained, in the others, 3-6 liters (about 90% hydrogen) of gas was formed.

The results are given in the table.

Results of Experiments on Alkaline Treatment of Lignin

Expt. No.	Amt. of alkali-insoluble product (%)	Amt. of carbon dioxide (%)	Precipitate formed on addition of acid						Ether extract from aqueous solution			Balance	
			Volatile acids calculated as CH_3COOH (%)		ether-soluble		ether-insoluble		total (% of sample taken)		Organic matter in residue (%)		
			total, %	total % of sample taken)	% of product	total % of sample taken)	% of product	total % of sample taken)	phenol (%)	acid (%)	—	—	—
1	None	—	7.2	4.3	12.5	30	30.5	70	11.2	—	—	4.1	23.7
2	0.5	10	13.2	43	25.8	60	17.2	40	25.0	—	—	6.0	40.8
3	7	10	19.6	37	27.7	75	9.3	25	27.0	7.2	20	6.3	45.9
4	6	9.9	18.6	36.2	26.6	74	9.6	26	23.4	7.1	16.3	8	4.1
												50	106.2

First, it should be noted that under our conditions the amounts of alkali-insoluble substances formed are much less than were obtained by Fischer (6-7% without a copper insert, 5% with the insert, with 15% caustic soda; Fischer found 16%). This justifies the use of lower temperatures and alkali concentrations. The purpose of the copper insert was shown by us earlier [11]; in a stainless-steel autoclave complex compounds insoluble in all reagents are formed from polyhydric phenols, iron, or chromium. Constant amounts of carbon dioxide (10%) and volatile acids (13-20%) are obtained under the given conditions, this shows that the primary products of alkaline hydrolysis of technical lignin undergo further changes. Acidification of the alkaline solution yielded a precipitate corresponding to 36-43% of the original lignin weight. 30-75% of this was soluble in ether. In the acid solution 6-8% of the lignin weight remained after ether extraction. The amount extracted by ether from it was 11-27%. The total amount of ether-soluble substances exceeded 50% in three of the experiments. All the products were almost free from methoxyl groups. In Experiments Nos. 3 and 4, all the reaction products are accounted for as accurately as possible; the weights were 111 and 106% on the lignin taken, which shows that water is involved in the reaction. The amounts of bound alkali (22 and 28% of the amount taken) are also accounted for in these experiments. Methyl alcohol was not considered or isolated, methoxyl losses were taken into account in the balance.

The precipitate formed on acidification, dried under vacuum at not over 40°, is completely soluble in acetone and alcohol, and 75% soluble in ether (gray powder). If heated in air at 100° and over it turns black and its solubility in organic solvents decreases. The molecular weight of the precipitate is 360-400 (in phenol). The ether-soluble portion is a fusible brown powder, molecular weight about 380; it contains C 75.0, H 6.3%.

The portion insoluble in ether is a black, infusible powder, incompletely soluble in alcohol and acetone; it contains 73% carbon and 5.4% hydrogen. The variability of these products when heated in presence of atmospheric oxygen shows that they are highly reactive. The mixture of phenols and acids, extracted by ether from acid aqueous solution, is a dark viscous liquid. The phenolic portion contains 68% carbon and 7.2% hydrogen;

the acid portion contains 50% and 5.8% respectively; the equivalent of the acid portion is 98; it contains 75% phenolic acids and 10% higher fatty acids. The acids volatile in steam contain 10% of higher fatty acids (equivalent 105, odor of caproic acid) and 90% of a mixture containing roughly equal amounts of formic and acetic acids.

The substances not extracted from aqueous acid solution are acids, probably of carbohydrate origin (% C 35.0; % H 4.6); they give lead salts insoluble in water.

These facts show that our views on the possible formation of a mixture of substances of relatively low molecular weight ($M \sim 360$ -400), even from the very highly condensed Scholler's technical lignin, by aqueous alkali treatment under the optimum conditions for alkaline hydrolysis of phenol ethers are fully justified.

EXPERIMENTAL

Lignin from one of the hydrolysis factories processing conifer woods (spruce, pine) was used for the treatment. It was washed with water to remove sulfuric acid and acetone to remove resins, and then dried under vacuum. It contained (in %): moisture 1.1, ash 2.0, OCH_3 9.1, carbohydrates 22.5, carbon 63.1, hydrogen 6.4. The conditions used in its alkali treatment are indicated above. The autoclave was brought up to the given temperature over a period of 1.5 hours. After the experiment the autoclave was removed from the heater, and the gas was collected in a gas holder during the cooling. The autoclave contents were discharged onto a suction filter, the residue was washed with water and dried at 105° (insoluble in alkali).

Treatment of the filtrate. The volume was measured and a portion taken for determination of volatile acids and free alkali. The rest of the filtrate was made acid to Congo red with hydrochloric acid, with stirring, and the carbon dioxide was collected in a gas holder. The residue was separated by suction, washed with water, and dried under vacuum at 40-60°. The dried material was extracted with ether in a Soxhlet extractor and separated into an ether-soluble and an ether-insoluble portion. The acid filtrate was exhaustively extracted with ether in a liquid extractor, ether was removed from the extract, and the residue was separated into phenols and acids in the usual way. The acid solution after extraction was evaporated to dryness under vacuum and extracted with absolute alcohol. After removal of the alcohol the residue was weighed. Formic and acetic acid were determined by the usual methods in a separate portion of the original filtrate. For estimation of the amount of higher fatty acids, the entire filtrate in a special experiment (No. 5, conditions as No. 4) was acidified and steam was blown through until the distillate became neutral. The distillate was neutralized with caustic soda, evaporated to dryness, dried at 160° and decomposed in dry ether by gaseous hydrogen chloride. Sodium chloride was separated off by suction and the filtrate was distilled. The temperature rose sharply after the acetic acid had distilled over. The distillation was then stopped and the residue was weighed.

SUMMARY

1. In the light of modern data on the structure of lignin it is predicted that low-molecular substances can be obtained from technical lignins by treatment with alkali solutions under the conditions of a method developed by us earlier for alkaline hydrolysis of phenol ethers.

2. This method was used to convert the most inert (highly condensed) Scholler's lignin into phenolic character of molecular weights not over 400. The yield of ether-soluble products was over 50% of the weight of lignin taken.

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SYNTHESIS OF ACETYLENE FROM CALCIUM CARBONATE

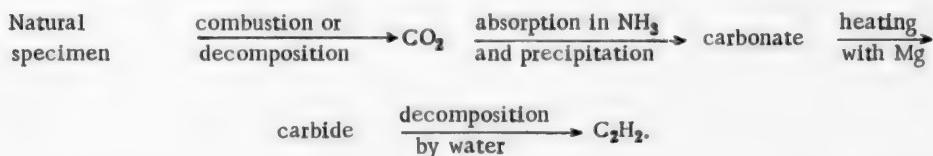
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The method for determination of radiocarbon, first developed by Libby [1] for estimation of the absolute geological ages of recent formations, is now being radically revised. In place of the method based on activity counts of solid carbon, new methods, based on more effective activity counts of gaseous carbon compounds (such as CO_2 , C_2H_2 , CH_4 , etc.) are being tested and introduced. Acetylene is the most suitable compound for this purpose. The advantage of acetylene is that its molecule contains two carbon atoms, and therefore a larger amount of carbon can be introduced into an equal volume used for the counting. In this connection, it is necessary to develop a simple method for preparation of acetylene with the minimum of radioactive contamination from carbon.

The problem reduces to synthesis of acetylene from CO_2 or carbonate, as the heat treatment of carbonaceous specimens used for age estimations involves formation of CO_2 by combustion of organic samples or decomposition of carbonates.

The proposed route of C_2H_2 synthesis may be represented as follows:



The preparation of carbonate from the natural specimens remains the same as in the method for preparation of solid carbon. Liberation of acetylene by the decomposition of alkali and alkaline-earth carbides with water is the simplest method for its preparation, and involves no difficulties. The most difficult stage in the whole scheme of acetylene synthesis is therefore formation of carbide from carbonate.

Various methods for preparation of carbides have been tested by a number of workers [2]. Not all these methods are suitable for the present purpose. For example, the carbides of alkali and alkaline-earth metals and magnesium are thermally unstable and begin to decompose into the elements even at relatively low temperatures (about 400°). For this reason such carbides cannot be prepared by the reactions of the corresponding carbonates with magnesium, as these reactions take place at higher temperatures (above 600°).

The use of lithium has been suggested for conversion of carbon from CO_2 into the carbide form [3, 4]. However, this method is inconvenient because it involves the use of considerable amounts of metallic lithium.

Carbides of the alkaline-earth metals are thermally stable, and therefore they can be used for preparation of acetylene from carbonates.

It is known that carbon of barium carbonate is converted into the carbide form when a mixture of BaCO_3 and metallic magnesium is heated [5]. Other alkaline-earth carbonates, including CaCO_3 , are not used for synthesis of acetylene, as since the time of Maquenne it has been assumed that the reaction of CaCO_3 with Mg

gives a very low percentage yield of carbide. It is not desirable to prepare acetylene, intended for determination of absolute geological ages by native C¹⁴, by conversion of the carbon in the specimen into BaCO₃, as Ba preparations are usually contaminated more than others with traces of radium. Therefore, the acetylene prepared with the aid of this reagent may be appreciably contaminated with radon.

Strontium carbide has recently been used for preparation of acetylene from SrCO₃, in view of the fact that the radium content is considerably lower in strontium than in barium preparations [6]. Passive removal of the radon, by keeping of the gas for several weeks before the count, is recommended.

We have reinvestigated the possibility of preparing carbide from carbon in CaCO₃, as calcium reagents are even less contaminated by radium, and are more resistant to carbon isotope exchange than the carbonates of barium and strontium.

The experiments were commenced by preparation of C₂H₂ from barium carbonate by the method described in [7]. By this method carbide is prepared by the action of heat at 950° on a briquetted mixture of BaCO₃ and metallic Mg powder in 5:2 ratio in a hydrogen atmosphere. The carbide formed is decomposed by water in a special gas generator. The acetylene yield reaches 85% on the original carbon.

For simplicity, it was decided not to use hydrogen for the reaction, but to conduct the reaction under vacuum. It was found during the experiments that the mixture need not be formed into tablets. The reaction mixture was densely tamped down in a steel tube fitted with a lid. This tube was placed in a steel pipe from which air was evacuated. The pipe was then heated in a tubular electric furnace to 950°. The average yield of acetylene was 80 ± 10% calculated on the original carbon.

In another series of experiments acetylene was prepared from calcium carbide. It is known that CaCO₃ has lower thermal stability than BaCO₃. We considered that a number of workers failed to obtain calcium carbide from mixtures of CaCO₃ with powdered Mg because of thermal decomposition of calcium carbonate at the instant of carbide formation, with consequent loss of CO₂. The thermal dissociation of CaCO₃ is represented by the equation



The effect of temperature on the equilibrium in thermal dissociation of CaCO₃ is shown by the following data.

Temperature (in °C)	550	600	650	700	750	800	850	897
CO ₂ pressure (mm)	0.4	1.8	6.9	22.2	63	167	372	760

The temperature of carbide formation lies in the 700–800° range, i.e., in the range of partial decomposition of calcium carbonate. To decrease decomposition of calcium carbonate it is necessary to prevent loss of CO₂ from the reaction space.

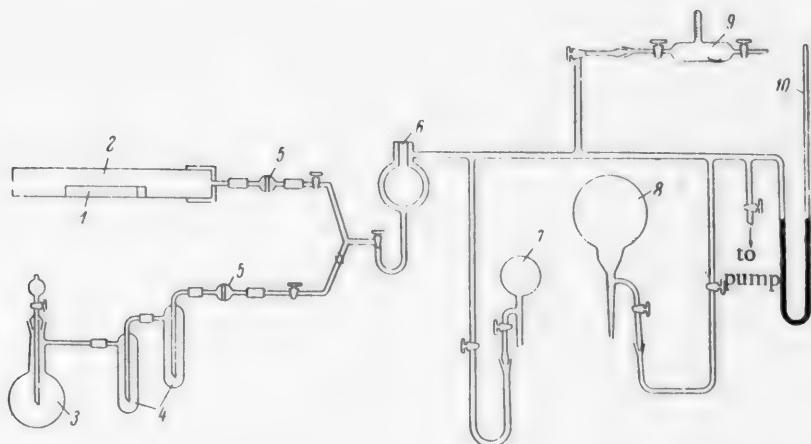
An experiment was therefore first performed on the carbidization of a mixture of CaCO₃ and Mg contained in a steel tube which was hermetically welded after being filled with the reaction mixture. Residual air was not removed from the tube. When the tube was heated to 700° carbonate was converted into carbide, with liberation of much heat. If the tube walls are less than 1 mm thick the gases formed in it may perforate the hot tube. The acetylene yield was about 80%.

Similar experiments were performed with tubes which were not welded but firmly stoppered by steel plugs, with different CaCO₃:Mg ratios.

The mixture was thoroughly ground and mixed and packed closely into a steel tube which was closed by a steel plug fixed by means of a cotter pin. This tube was placed in a horizontal steel pipe, welded hermetically at one end, and attached to a vacuum installation through a ground-joint condenser at the other. The whole system was evacuated while heated to 400°. The pipe was then rapidly heated to 900°. The manometer indicated evolution of a small amount of gas (CO₂ and remains of the air adsorbed by the powder) which was pumped out. The reaction of carbide formation proceeds according to the equation



Observations of the course of the reaction showed that when a definite temperature (about 700°) is reached carbidation occurs instantaneously and is accompanied by liberation of much heat. This results in a sharp rise of temperature. The pipe was cooled to room temperature and dismantled, and the contents of the inner tube were transferred, without grinding, into an ordinary Würtz flask attached to a vacuum installation (see diagram).



Apparatus for preparation of acetylene. 1) Tube with reaction mixture; 2) steel pipe with attached condenser; 3) flask for preparation of C_2H_2 ; 4) trap for freezing moisture; 5) porous glass filter; 6) trap for freezing C_2H_2 ; 7) storage sphere for small amounts of C_2H_2 (0.5 liter); 8) storage sphere for large amounts of C_2H_2 (5 liters); 9) gas pipet for C_2H_2 sampling; 10) manometer.

After this system had been evacuated, water was added dropwise into the flask through a dropping funnel. The acetylene formed passed through two traps immersed in a mixture of solid carbon dioxide and acetone, to collect moisture, and frozen in a trap cooled in liquid nitrogen. The decomposition of carbide by water was continued for about 30-45 minutes. Nearly all the acetylene was liberated during this period. Not more than 3-5% of the acetylene was additionally liberated after 24 hours. The formation of acetylene was accompanied by liberation of hydrogen as the result of a reaction between excess Mg and water. This hydrogen was pumped out at intervals. At the end of the reaction the acetylene was defrosted and collected in a storage sphere. The amount of acetylene formed in the system of known volume was found from the manometer readings. The average acetylene yield calculated on the carbon initially taken was $86 \pm 6\%$. The acetylene was tested for purity, i.e., for presence of other gases, by means of K_2HgI_4 solution [8]. A special 25 ml gas pipet with a side tube graduated to 0.1 ml was adapted for this purpose. The pipet was evacuated and a sample of the prepared acetylene was collected in it. The pipet was then disconnected from the system and immersed in the mercuric iodide absorbent solution. The liquid filled the pipet completely. This showed that our acetylene was free from gaseous impurities.

It was subsequently found that the use of vacuum in the carbidization process is equally unnecessary.

In the next series of experiments carbide was prepared by the action of heat on mixtures of carbonates with magnesium in air. The experiments were performed with $BaCO_3$ and $CaCO_3$, mainly the latter. The reaction mixture was put in steel tubes with close-fitting steel bungs. The tubes were heated in air by means of a burner, or in a tubular steel furnace. Carbide formation was again observed at about 700°, and took place very rapidly (not more than 1 minute). At the instant of carbide formation, gases (CO_2 , Mg vapor) escaped through the gap between the tube and the bung, and caught fire. Carbon monoxide and amorphous carbon were found in the reacted mixture, so that the yield of acetylene was incomplete. The tube was then heated for a short time to 900° to ensure complete reaction of the whole mixture. This operation usually resulted in the steel bung being welded to the tube by melted magnesium. The heated tubes were cooled in water for speedier removal of the carbide from them.

The reaction product — a mixture containing CaC_2 , MgO , CaO , C, and Mg — was transferred to the flask for acetylene formation. The average yield was $71 \pm 2\%$ for BaCO_3 , and $74 \pm 8\%$ for CaCO_3 .

These results were close to those obtained in experiments on the preparation of carbide under vacuum.

The advantage of the process performed in air is that it is simpler and more rapid.

Thus, the preparation of acetylene from carbonates, and therefore, from carbon in a specimen, proves to be a very simple operation which requires about 10 minutes for the carbidization and about 2 hours for isolation and purification of acetylene.

In most of the experiments the amount of carbonate taken contained 0.6 g of carbon. When the scale of the process was raised to 2 g of carbon, the yield of carbide and therefore of acetylene was further increased. The effect of increasing the amount of Mg in the reaction mixture was tested. No significant differences in the acetylene yield were found.

The only defect of the method described for synthesis of acetylene from calcium carbonate is the variability of the yield, which fluctuated considerably in duplicate experiments (see table). The cause lies in losses of carbon in the form of CO_2 , CO, and amorphous carbon during carbide formation.

The acetylene yields in the experiments are summarized in the table.

Results of Experiments on Acetylene Synthesis

Carbon : magnesium ratio	Carbidization under vacuum				Carbidization in air			
	BaCO_3		CaCO_3		BaCO_3		CaCO_3	
	carbonate mag-nesium ratio	C_2H_2 yield (%)						
1 : 6.7	5 : 2 {	74	5 : 4 {	89*	5 : 2 {	75	5 : 4 {	62
		83		98		67		70
		94		80		—		64
		97		77		—		—
		89		—		—		—
1 : 8.3	—	—	—	—	—	—	5 : 5 {	75
		—		—		—		77
		—		—		—		86 **
1 : 10	5 : 3 {	70	5 : 6 {	88	5 : 3	70	5 : 6 {	68
		70		76		—		62
		67		81		—		59
1 : 11.7	—	71	5 : 7 {	86	5 : 7	—	5 : 7	80
		—		87		—		77
		—		98		—		—
1 : 13.3	—	—	—	—	5 : 4	72	5 : 8	82
1 : 16.7	5 : 5	90	—	—	—	—	—	85
1 : 20	5 : 6	74	—	—	—	—	—	—
Average		80 ± 10		86 ± 6		71 ± 2		74 ± 8

* A sealed steel tube was used for carbidization in this experiment.

** These experiments were performed with increased amounts of carbon, calculated to yield 2 liters of C_2H_2 .

SUMMARY

It is shown that calcium carbide (and therefore acetylene) can be prepared from CaCO_3 by the action of heat on a mixture of $\text{CaCO}_3 + \text{Mg}$ in a firmly closed steel tube at about $700\text{--}800^\circ$. It is not necessary to perform the reaction in a current of hydrogen, or in a sealed tube, or under vacuum; this makes the process much more simple and rapid.

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SYNTHESIS OF DETERGENTS FROM SYNTHINE HYDROCARBONS

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One type of active detergents consists of sodium alkylbenzene sulfonates, which may be synthesized from appropriate petroleum fractions or from synthetic liquid fuel, such as synthine [1-5]. The detergent properties of these compounds depend both on the number of carbon atoms in the alkyl chain and on its structure. The detergent properties improve with chain length up to a certain maximum, and then worsen because of decreased solubility in water. The optimum lies between 12 and 15 carbon atoms in the side chain. Branched alkyl chains are undesirable, as they lower detergent properties and make the substances hygroscopic.

Sulfonates are obtained in the form of a dark brown pasty mass. To improve the detergent properties and appearance of the product, sodium sulfate is added to a solution of the sulfonate, which is then evaporated to dryness, yielding a white or pale yellow powder which usually contains 30-40% of sodium alkylbenzene sulfonate and 60-70% of sodium sulfate.

The purpose of the present work was synthesis of sodium alkylbenzene sulfonates from synthine hydrocarbons made in presence of the usual cobalt catalysts, and tests of these salts as surface-active agents and detergents. The synthine was first hydrogenated and then separated into fractions from C₆ to C₁₇, which were chlorinated to monochlorides. These were used for alkylation of benzene in presence of aluminum chloride, and the monoalkylbenzenes were then converted into sodium alkylbenzene sulfonates, aqueous solutions of which were tested for detergency.

EXPERIMENTAL

Synthine, washed three times with 10% NaOH solution and dried over anhydrous copper sulfate, was hydrogenated at room temperature and atmospheric pressure over platinized carbon with added H₂PtCl₆, and then distilled over metallic sodium. The properties of the hydrogenated synthine fractions are given in Table 1. The bromine numbers of these fractions ranged from 0.3 to 1.8.

From other portions of the hydrogenated synthine broad C₁₀ to C₁₂, C₁₃ to C₁₇ and C₁₀ to C₁₇ fractions were obtained by distillation; their properties are also given in Table 1. The hydrogenated-synthine fractions were chlorinated in presence of iodine (0.5% on the weight of the fraction) at 60-70° in diffuse daylight; chlorine was passed until the weight increase of the reaction mass corresponded to monochloride formation (Table 1).

For the alkylation reaction, the chloride formed was added to a mixture of benzene and anhydrous aluminum chloride, the weight proportions of monochloride, benzene, and AlCl₃ being 1:6:0.1. The mixture was stirred for 3 hours at 40-50°. At the end of the reaction the resin formed was removed, the residue was washed with water, 10% aqueous NaOH, and water again, and the unconverted benzene was distilled off. The alkylation product was distilled from a Favorskii flask under vacuum to give three fractions, one of which was free from alkylation products, the second consisted mainly of monoalkylbenzenes, and the third contained more complex alkylation products.

Data on the monoalkylbenzene fractions obtained are summarized in Table 2.

The data in Table 2 indicate that the physical constants of the alkylation products obtained from the broad C₁₀ to C₁₂ fraction, and especially from the C₁₀, C₁₁, and C₁₂ fractions, are somewhat high. This is probably due to the presence of an admixture of diphenylalkanes formed from dichlorides, which were obtained in a relatively large amount because of the longer chlorination time used for these hydrogenated-synthine fractions (Table 1).

TABLE 1
Chlorination of Hydrogenated-Synthine Fractions

Hydrogenated-synthine fraction				Chlorination			
C _n of fraction	boiling range (in °C)	n ²⁰ _D	d ²⁰ ₄	wt. of original fraction (g)	reaction time (hours)	yield of chloride (g)	yield of chloride (% on monochloride)
C ₈	100—126	1.3960	0.6974	40.0	1.5	42	81
C ₉	126—151	1.4035	0.7110	50.2	1.5	55	86
C ₁₀	151—174	1.4088	0.7247	83.9	13.0	120	114
C ₁₁	174—200	1.4154	0.7310	86.0	11.0	141	134
C ₁₂	200—216	1.4205	0.7384	50.0	4.0	86	143
C ₁₃	216—236	1.4242	0.7549	53.7	2.0	64	100
C ₁₄	236—254	1.4282	0.7654	35.4	1.3	42	100
C ₁₅	254—270	1.4315	0.7710	22.0	1.0	26	100
C ₁₆	270—280	1.4335	0.7754	12.4	0.7	14	100
C ₁₇	280—303	1.4360	0.7799	28.9	1.0	32	100
C ₁₀ —C ₁₂	150—216	1.4178	0.7392	97.4	4.0	119	99
C ₁₃ —C ₁₇	216—300	1.4302	0.7643	114.0	2.2	132	100
C ₁₀ —C ₁₇	150—300	1.4280	0.7467	221.0	2.2	262	100

TABLE 2
Alkylation of Benzene by Monochlorides and Sulfonation of the Alkylation Products

Alkylation products from C _n synthine fraction and benzene				Yield of Na sulfonates (% on alkylation product)	
C _n of alkyl group	Boiling range (in °C)	n ²⁰ _D	d ²⁰ ₄	yield (% on monochloride)	
C ₈	120—240 (at 760 mm)	1.4686	0.8275	34.8	—
C ₉	124—147 (21)	1.4833	0.8560	19.8	87.6
C ₁₀	120—150 (9)	1.4949	0.8808	37.2	92.0
C ₁₁	140—190 (13)	1.5053	0.9331	22.7	105.9
C ₁₂	140—200 (2)	1.5280	1.0025	31.7	102.0
C ₁₃	115—175 (1.5)	1.4873	0.8656	39.4	94.0
C ₁₄	115—175 (1.5)	1.4862	0.8698	41.9	90.3
C ₁₅	115—200 (3)	1.4810	0.8577	37.0	75.4
C ₁₆	115—200 (3)	1.4600	0.8425	26.0	71.2
C ₁₇	115—225 (1)	1.4721	0.8441	42.0	96.1
C ₁₀ —C ₁₂	105—225 (2)	1.4968	0.8876	36.4	88.8
C ₁₃ —C ₁₇	140—230 (2)	1.4900	0.8766	29.0	92.0
C ₁₀ —C ₁₇	130—230 (2)	1.4878	0.8830	27.8	102.0

Sulfonation of the monoalkylbenzene fractions (Table 2) was usually performed as follows: the alkylation product was first stirred for an hour with 5% (by weight) of H₂SO₄ (d = 1.84). The liquid was left to settle, the acid was poured off, and 110% (by weight) of H₂SO₄ of the same strength was added at once, with stirring, this was followed by gradual addition, during 1 hour, of 200% (by weight) of 7.5% oleum. The temperature of the

reaction mixture was maintained at 30-40°. After all the oleum had been added the stirring was continued for 1 hour, and 100% of water (on the volume of the original alkylation product) was then added; the temperature of the mixture rose to 60-70°. After the liquid had settled, the lower acid layer was poured off and 120% of water (on the weight of the alkylation product) was added with stirring. The solution was neutralized at 60-70° with 10% aqueous NaOH solution and 170% (on the weight of the original alkylation product) of dry Na₂SO₄ was added; the solution was then evaporated to dryness. The yield of sodium alkylbenzene sulfonates was 90-100% calculated on the original alkylation product (Table 2).

The evaporated product was a white or yellowish powder, and contained 25-40% sulfonates and 75-60% Na₂SO₄.

The surface activities and detergent properties of aqueous solutions of some samples are given in Tables 3 and 4.

TABLE 3
Surface Activity and Detergent Properties of Aqueous Solutions of Individual
Alkylbenzene Sulfonates Prepared from Synthine Hydrocarbons Made in
Presence of Cobalt Catalyst

Alkylbenzene sulfonate from fraction of C ₁₁	Solution conc. (%)	Solution pH	Wetting power, cos θ	Surface tension (ergs/cm ²)	Detergent effect (%)
C ₉	0.5	2.7	0.72897	36.0	200.0
	0.25	2.8	0.72236	40.4	161.0
	0.125	3.0	0.58779	46.5	130.7
	0.5	8.4	0.87882	33.1	228.0
	0.25	8.0	0.84104	33.3	264.3
	0.125	7.7	0.70091	43.2	257.1
C ₁₀	0.5	3.7	0.87178	37.8	230.7
	0.25	3.8	0.82511	38.8	284.6
	0.125	3.9	0.81748	39.9	176.9
	0.5	3.9	0.90631	31.8	305.7
	0.25	8.5	0.88285	33.9	307.1
	0.125	8.2	0.86603	39.2	285.1
C ₁₂	0.5	9.8	0.89101	36.9	305.7
	0.25	9.7	0.89603	37.5	228.5
	0.125	9.6	0.83147	38.4	221.0
C ₁₃	0.5	9.6	0.92050	27.5	301.4
	0.25	8.4	0.89687	29.6	293.0
C ₁₆	0.5	2.2	0.80920	43.9	269.5
C ₁₇	0.5	2.7	0.78532	46.3	270
	0.25	2.9	0.76041	48.0	303
	0.125	3.0	0.69466	53.0	284

The following methods were used for determinations of surface activity and detergent properties of aqueous solutions of alkylbenzene sulfonates.

For determination of foaming power, 50 ml of solution of a known concentration was shaken in a 250 ml cylinder for 2 minutes (50 shakings). The foam volume was measured immediately after the end of the shaking, after 8 seconds, and after 3 and 6 minutes. Foam stability was found from changes in volume, and foam structure was evaluated visually from the cell size as "compact" or "loose."

Surface tension of the solutions was determined by means of the Traube stalagmometer; the emulsifying power, by Rebinder's method from the stability of emulsions formed by the solutions with benzene; and the wetting power, from the cosine of the contact angle, determined by means of Rebinder's apparatus.

The detergent effect of aqueous alkylbenzene sulfonate solutions was determined by experimental launderings of artificially soiled specimens of cotton fabric of definite size. The launderings were performed in a

Launderometer in 100 ml of test solutions of known concentrations. The laundered fabric was rinsed twice in water, dried, ironed, and examined photometrically. The detergent effect was calculated as a percentage of the detergent effect of water on the artificially soiled fabric, the latter effect being taken as 100%.

TABLE 4

Surface Activity and Detergent Properties of Aqueous Solutions of Individual Groups of Alkylbenzene Sulfonates

Alkylbenzene sulfonate from fraction of C _n	Solution conc. (%)	Solution pH	Wetting power, cos θ	Surface tension (ergs/cm ²)	Detergent effect (%)		
					cotton fabric	wool	rayon
C ₁₀ —C ₁₂	0.5	7.0	0.78801	27.48	255.0	222.2	175.0
	0.25	7.0	0.69466	31.78	238.2	250.0	162.5
	0.125	7.0	0.57358	47.35	206.3	271.1	212.5
	0.06	7.0	0.51877	55.77	202.5	155.5	112.5
	0.03	7.1	0.45917	66.05	157.0	155.5	112.5
	0.015	7.1	0.45787	69.72	165.4	155.5	106.5
C ₁₃ —C ₁₇	0.5	8.0	0.87882	31.37	—	—	—
	0.25	7.7	0.85416	32.17	—	—	—
	0.125	6.9	0.80730	33.90	—	—	—
	0.06	6.6	0.79335	38.02	—	—	—
	0.02	6.5	0.75280	43.27	—	—	—
	0.015	6.4	0.66480	53.40	—	—	—
C ₁₀ —C ₁₇	0.5	8.2	0.88902	31.37	—	—	—
	0.25	7.2	0.86384	33.02	—	—	—
	0.125	6.7	0.83629	38.90	—	—	—
	0.06	6.6	0.78801	37.46	—	—	—
	0.03	6.5	0.71896	44.03	—	—	—
	0.015	6.4	0.68200	52.28	—	—	—

Resistance of the alkylbenzene sulfonate to water hardness was determined by titration of 100 ml of water of 15° hardness with 1% solution of the test substance, and calculated in milliliters of 1% test solution.

Aqueous (0.125–0.5%) solutions of products obtained from synthine fractions between C₁₀ and C₁₅, and also from C₁₃ to C₁₇ and C₁₀ to C₁₇ fractions, have good emulsifying power, while aqueous solutions of products from fractions between C₉ and C₁₃ inclusive have good resistance to hard water (over 100 ml). The foaming power of

solutions obtained from fractions between C₉ and C₁₅ inclusive (and from the broad C₁₀ to C₁₇ fraction) is characterized by high foam volumes (at 20°, 265–275 ml initially, 150–220 ml after 6 minutes) and a compact microcellular foam structure. The foaming power of products obtained from C₁₆ and C₁₇ fractions is lowered considerably at 20° and increases with increase of temperature up to 60°. Increase of pH (from an acid to an alkaline medium) improves the surface-active properties of the solutions: the surface tension, and wetting and emulsifying power.

The alkylbenzene sulfonate made from the broad C₁₀ to C₁₇ synthine fraction had better emulsifying power and resistance to hard water than samples made from the individual narrower C₁₀ to C₁₂ and C₁₃ to C₁₇ fractions.

TABLE 5
Detergent Effect of Soap

Solution conc. (%)	Detergent effect (%)
0.5	220
0.25	230
0.125	200
0.06	180
0.03	180

It follows from Tables 3 and 4 that the synthesized Na alkylbenzene sulfonates have detergent power in acid and alkaline media, the effect being greater in alkaline media.

For comparison of these alkylbenzene sulfonates with ordinary soap, the detergent effect of aqueous solutions of the latter was determined under the same conditions with the use of cotton fabric (Table 5).

Comparison of the data in Table 5 with the results obtained for alkylbenzene sulfonates (Tables 3 and 4) indicates that aqueous solutions of the latter are not inferior to soap solutions in their detergent power, and are even better in some cases. It must also be taken into account that aqueous solutions of alkylbenzene sulfonates have the following advantages over soap: they can be used at lower temperatures, in acid or alkaline media, and in hard water, without undergoing hydrolysis.

S U M M A R Y

1. Sodium alkylbenzene sulfonates, which have the properties of surface active agents and detergents, were prepared from C₈ to C₁₇ hydrocarbons of hydrogenated synthine.

2. In view of the surface activity and detergent properties of these substances, they may be used in the production of fatless wetting agents and detergents under suitable conditions with regard to raw-material supplies and process economics.

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SYNTHESSES OF SOME THIOPHENE DERIVATIVES AND STUDIES OF THEIR BEHAVIOR AS RUBBER INGREDIENTS (ACCELERATORS AND ANTIOXIDANTS)

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The increasing demands being made on rubber products, improvements in their manufacturing processes, and the increase in the range of available rubbers have necessitated extensive investigations directed toward searches for new types of vulcanization accelerators for rubbers, and antioxidants for raw and vulcanized rubbers.

Many compounds suitable for these purposes are now known, but the behavior of certain classes of heterocyclic compounds, including those of the thiophene series, as rubber ingredients has been studied little. It is known from the literature (mainly foreign patents) that such compounds may be used as ingredients of rubber mixes [1, 2]. It should be noted in this connection that the so-called thiophene concentrate, extracted from natural gasoline and Kashpir shale tar [3], is a possible source of thiophene and especially of its simplest homologs.

In this paper we describe the preparation and tests, as rubber ingredients, of 15 compounds of the thiophene series containing the azomethine group, of the general formula $\text{XC}_4\text{H}_2\text{SCH}=\text{NRY}$, where X is hydrogen or CH_3 , R is an aliphatic or aromatic radical, and Y is a substituent. Azomethines with a benzene ring were also synthesized in order to compare their behavior as vulcanization accelerators with their analogs from the thiophene series. In addition, 5 secondary amines of the type $\text{C}_4\text{H}_5\text{SCH}_2-\text{NHR}'\text{X}$, where R' is an aromatic radical and X is a substituent, were prepared and tested. In addition to the azomethine compounds and secondary amines of the thiophene series, 2-mercapto-4-(2'-thienyl)thiazole and 2-(2'-thienyl)pyrimidazole (the latter synthesized by us) were tested.

EXPERIMENTAL

Azomethines ($\text{RCH}=\text{NR}'$) were prepared by boiling of equimolecular amounts of aldehyde (2-thiophenaldehyde, 2-methyl-5-thiophenaldehyde) in benzene with the corresponding amine until the volume of the water formed became constant [1]. In nearly every instance the reaction took place within 1.5-2 hours with yields up to 80-85%, calculated on the reaction product, or about 85-90% calculated on the water formed. An exception in this respect is provided by 2-phenyldene-p-nitroaniline, the yield of which did not exceed 12%; this may be attributed to the influence of the electron-accepting substituent in the para position. After evaporation of the benzene the reaction product was distilled under reduced pressure or crystallized. Some compounds (2-phenyldene-p-aminophenol, bis(2-phenyldene)ethylenediamine, 5-methyl-2-phenyldene-p-aminophenol) were also prepared by boiling in ethyl alcohol for 15 minutes [4]; the alcoholic solution was then poured onto ice and the separated reaction product was filtered off and purified by crystallization.

The boiling points, melting points, yields, and analytical data of the azomethine compounds are given in Table 1.

The reaction of 2-thiophenaldehyde with 2-aminopyridine performed at the boil in benzene solution yielded $\text{N},\text{N}'-(2'-phenyldene)\text{bis}-2\text{-aminopyridine}$:



TABLE I
Azomethine Compounds of the General Formula RCH=NR'

Compound No.	R	R'	Temperature (in °C)		Composition	Contents (%)				
			b. p.	m. p.		calculated				
						C	H	N	C	
I	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_5\text{CH}_3$ (o)	141—143 (4 mm) ^a	—	$\text{C}_{11}\text{H}_9\text{NS}$	—	7.48	—	—	
II	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{CH}_3$ (p)	162—163 (9 mm)	—	$\text{C}_{12}\text{H}_{11}\text{NS}$	71.65	5.47	—	7.60	
III	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{Cl}$ (p)	—	59—60 b	$\text{C}_{12}\text{H}_{11}\text{NS}$	—	—	—	—	
IV	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{OCH}_3$ (p)	—	69—69.5	$\text{C}_{12}\text{H}_8\text{ClNS}$	—	—	—	7.00	
V	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{OH}$ (p)	—	45—46 c	$\text{C}_{12}\text{H}_{11}\text{NOS}$	—	—	—	6.46	
VI	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{NO}_2$ (p)	—	203—204 b	$\text{C}_{11}\text{H}_8\text{NOS}$	—	—	—	6.63	
VII	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{NO}_2$ (m)	—	131.5—132.5 b	$\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2\text{S}$	—	—	—	—	
VIII	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{C}_6\text{H}_4\text{NO}_2$ (m)	—	112—113 b	$\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2\text{S}$	—	—	—	12.08	
IX	$\text{C}_4\text{H}_3\text{S}$ (2)	C_6H_7 (β)	—	107—108 b	$\text{C}_{15}\text{H}_{11}\text{NS}$	—	—	—	12.16	
X	$\text{C}_4\text{H}_3\text{S}$ (2)	$\text{CH}_2\text{CH}_2\text{OH}$	146—147 (6 mm) ^f	—	$\text{C}_{15}\text{H}_{11}\text{NOS}$	75.95	4.64	—	—	
XI	$\text{C}_4\text{H}_3\text{SCH}=\text{NCH}_2$ ₂	$\text{CH}_2\text{CH}_2\text{OH}$	—	89—91 b	$\text{C}_7\text{H}_9\text{NOS}$	—	—	—	—	
XII	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	C_6H_5	—	76	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2$	—	—	—	8.95	
XIII	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_4\text{OCH}_3$ (p)	—	60—61 b	$\text{C}_{12}\text{H}_{11}\text{NS}$	—	—	—	—	
XIV	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_4\text{OH}$ (p)	—	87	$\text{C}_{12}\text{H}_{11}\text{NOS}$	—	—	—	—	
XV	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_2\text{CH}_2\text{OH}$	—	76—77	$\text{C}_{13}\text{H}_{13}\text{NOS}$	—	—	—	7.10	
XVI	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_4\text{OH}$ (p)	—	225—226	$\text{C}_{12}\text{H}_{12}\text{NOS}$	—	—	—	6.03	
XVII	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_2\text{CH}_2\text{OH}$	—	80	$\text{C}_8\text{H}_{11}\text{NOS}$	56.78	—	—	6.22	
XVIII	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_4\text{OCH}_3$ (p)	120—121 (4 mm) ^h	74	$\text{C}_{14}\text{H}_{13}\text{NO}$	—	—	—	—	
XVII	$\text{C}_4\text{H}_2\text{SCH}_3$ (2,5)	$\text{C}_6\text{H}_2\text{CH}_2\text{OH}$	—	69—70 b	$\text{C}_{13}\text{H}_{11}\text{NO}$	—	—	—	—	
XVII	C_8H_5	$\text{C}_6\text{H}_4\text{OCH}_3$ (p)	—	181—182.5 b	$\text{C}_9\text{H}_{11}\text{NO}$	—	—	—	—	
XVII	C_6H_5	$\text{CH}_2\text{CH}_2\text{OH}$	112—115 (4 mm) ⁱ	—	$\text{C}_{12}\text{H}_{11}\text{NO}$	72.45	7.43	—	—	
XVII	C_6H_5	$\text{CH}_2\text{CH}_2\text{OH}$	161—162 (29 mm)	—	$\text{C}_{12}\text{H}_{11}\text{NO}$	—	—	—	7.37	

a) By [6], b. p. 122—125° (2 mm); b) from ethyl alcohol; c) from heptane; d) by [1], m. p. 204—205° (from ethyl alcohol); e) found %: S 13.45, calculated %: S 13.50; f) $n^{20}\text{D}$ 1.6042; g) by [1], m. p. 90—91° (from benzene-hexane mixture, see also [4], m. p. 92° from dil. alcohol); h) $n^{20}\text{D}$ 1.5960, found %: S 18.94; calculated %: S 18.92; i) by the data of Bergmann et al. [7], b. p. 161—162° (30 mm); $n^{20}\text{D}$ 1.5729, benzylidene structure demonstrated by molecular refraction and infrared spectrum; by West's data [8], b. p. 128—130° (2 mm); $n^{20}\text{D}$ 1.5572.

After removal of the reaction water under reduced pressure (at 9-10 mm) the reaction product was transferred to a filter and washed with heptane; the yield of product with m. p. 66-67° was about 50% calculated on the aldehyde. After three crystallizations from benzene - heptane mixture (1:3) the melting point was 79-80°.

Found %: C 64.14, 64.21; H 4.98, 4.87; S 12.14. $C_{15}H_{14}N_4S$. Calculated %: C 64.40; H 4.94; S 12.14.

According to Kaye and Kogon [5], 2-(2'-thenylidene)aminopyridine (b. p. 110–112° at 0.03 mm) is obtained in 71% yield when equimolecular amounts of 2-thiophenaldehyde and 2-aminopyridine are boiled in cumene solution (boiling point 153°).

Our experiments confirmed again that bisamino compounds are decomposed with formation of azomethine compounds if the temperature of the reaction mixture is above the melting point of the given bisamino compound [5, 9].

Secondary amines [$\text{RCH}_2-\text{NHR}'$] were prepared mainly by heating of phenyl dichloride with amines in solutions of anhydrous benzene or toluene in presence of condensing agents (potash, pyridine, etc.) [2]. The reaction is usually accompanied by formation of considerable amounts of a tertiary amine (Method A). In some cases we used reducing alkylation of the reaction products of amines with 2-thiophenaldehyde in presence of formic acid [10]. The reaction was sometimes complicated by formylation of the secondary amine formed; the formyl group was removed by saponification by means of alcoholic alkali.

Reduction of azomethine compounds by the action of magnesium in methyl alcohol was also tried [11]; however, this method did not give the desired results.

2-Phenyl-4'-methoxyphenylamine (Method A). A solution of 39 g of phenyl dichloride (b. p. 64-66° at 13 mm) in 60 ml of toluene was added at 80-85° during 2.5 hours to a solution of 36.5 g of p-anisidine and 28.5 g of anhydrous pyridine in 150 ml of dry toluene. The mixture was then heated with moderate boiling of the solution for 2 hours. The mixture was cooled and toluene was decanted from the resinous residue; after decomposition by water, the reaction product was extracted from the residue by means of toluene. The combined toluene solution was washed with water and with alkali solution, dried, and distilled. After removal of toluene, the following fractions were collected: first fraction of b. p. 173-180° (4 mm, 19.7 g), and second fraction of b. p. 212-215° (4 mm, 14.2 g). A second distillation of the first fraction yielded 13.7 g of 2-phenyl-4'-methoxyphenylamine, b. p. 160-162° (3 mm), m. p. 59-61°.

Found %: C 66.03, 65.69; H 5.97, 6.02; S 15.26, 14.96. $C_4H_9SCH_2HNC_6H_4OCH_3$. Calculated %: C 65.70; H 5.98; S 14.62.

A second distillation of the second fraction yielded 10.6 g of bis(2-phenyl)-4'-methoxyphenylamine, b. p. 208-210° (4 mm).

Found %: C 64.99, 65.14; H 5.51, 5.49; S 19.74, 19.67. $(C_4H_9SCH_2)_2NC_6H_4OCH_3$. Calculated %: C 64.75; H 5.39; S 20.31.

The secondary amines made by Method A, their boiling and melting points, yields, and analytical data are given in Table 2.



2-(2'-thienyl)pyrimidazole (**XXV**) was synthesized by the action of 2-chloroacetylthiophene on 2-amino-pyridine by the following procedure [14]: a mixture of 1.88 g of 2-aminopyridine, 3.2 g of 2-chloroacetyl-thiophene (b. p. 110–112°, 3 mm) and 2 g of sodium bicarbonate in 40 ml of water was stirred for one hour at room temperature. After standing for 12 hours the mixture was heated to 90°. The oil which solidified on cooling was transferred to a filter, washed with water, and dried in a vacuum desiccator. The product (3.3 g) was extracted 4 times with 50 ml lots of ether. After evaporation of the ether to a small volume pale yellow crystals

TABLE 2
Secondary Amines of the General Formula RCH_2-NR' Prepared by Method A

Compound No.	R	R'	Boiling point (in °C)	Yield (%)	Composition	Contents (%)			
						calculated		found	
	C	H	N	C	H	N			
XIX	C_4H_3S (2)	C_6H_5	132-134 (4 mm)	50	$C_{11}H_{11}NS^*$	-	-	7.41	-
XX	C_4H_3S (2)	$C_6H_4CH_3$ (o)	134-136 (4 mm)	45	$C_{12}H_{13}NS$	70.90	6.41	-	7.53
XXI	C_4H_3S (2)	$C_6H_4OCH_3$ (p)	160-162 (3 mm)	~25	$C_{12}H_{13}NOS^{**}$	65.70	5.98	-	-
XXII	C_4H_3S (2)	C_6H_4Cl (p)	154-155 (4 mm)	54	$C_{11}H_{10}NClS^{***}$	59.05	4.50	6.26	6.47
XXIII	C_4H_3S (2)	$C_{10}H_7$ (β)	195-197 (3 mm)	11.3	$C_{15}H_{13}NS^{****}$	-	-	5.84	-

* n_D^{20} 1.6250, b. p. 174-178° (11 mm), N-formyl-N-phenylamine, m. p. 73.5-74.5° (found %: N 6.64, 6.63; for $C_{12}H_{11}NOS$ calculated %: N 6.49). By [2] for 2-phenylphenylamine b. p. 135-150° (2-3 mm).

** Calculated %: S 14.62; found %: S 15.11; in addition, about 15% of bis(2-phenyl)-4-methoxyphenylamine of b. p. 208-210° was formed.

*** A tertiary amine of the composition $(C_4H_3SCH_2)_2NC_6H_4Cl$ was also isolated in about 28% yield, b. p. 217-219° at 5 mm (found %: N 4.61; calculated %: N 4.38).

**** When gaseous HCl was passed into a benzene solution a salt of the composition $C_4H_3SCH_2NHCl_2$ was obtained; neutralization equivalent, found : 276.2; calculated : 275.5. McCracken [2] gives b. p. 195-210° (1.5 mm) for 2-phenyl-2-naphthylamine.

(2 g) were obtained, m. p. 137-138°; crystallization from 170 ml of heptane gave pale yellow needles of m. p. 137.5-138°.

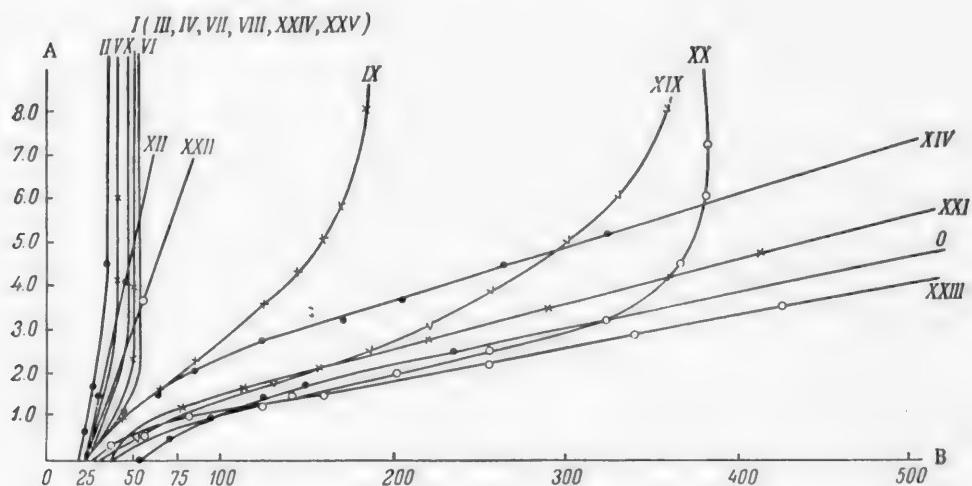
Found %: C 65.98, 66.02; H 4.09, 4.00; S 16.05, 16.17. $C_{11}H_8N_2S$. Calculated %: C 66.00; H 4.00; S 16.00.

In conclusion of this part of the paper it must be pointed out that of the thiophene derivatives listed in this communication the following compounds were synthesized by us: II-V, VII-X, XII-XV, XX-XXII, and XXV.

Results of Tests of Thiophene Derivatives as Antioxidants

It is known that the main cause of thermal aging of raw and vulcanized rubbers is oxidation of polymer molecules by atmospheric oxygen. The oxidation of rubbers in absence of antioxidants is now regarded as a radical chain process with degenerate branching. The kinetics of oxygen addition to rubber at elevated temperatures (above 100°) can be represented by autocatalytic curves [15].

Antioxidants introduced into raw or vulcanized rubbers to protect them against aging are inhibitors of the chain reactions. By terminating the oxidation chains they prevent their branching and thereby sharply change the character of the process: in presence of antioxidants rubber is oxidized at a constant, relatively low rate, i.e., the so-called "induction period" appears. The oxidation rate during the induction period, and the duration of the latter, determine the aging rate of the raw or vulcanized rubber [16]. In their turn, these parameters are determined, under equal conditions, by the inhibiting power of the antioxidant present in the system and are therefore the most rational characteristics for evaluation of its effectiveness.



Kinetic curves for the oxidation of rubber in presence of various compounds. A) Amount of oxygen absorbed (ml/g); B) time (minutes).

In the present investigation we estimated the inhibiting effects of the compounds described above on the oxidation of sodium butadiene rubber at 130°. The synthesized compounds were introduced into the technical rubber on microrolls, 2.5 millimole being taken per 1 mole of rubber. The rubber did not contain any other antioxidants. The mixture was molded into plates 0.25-0.35 mm thick, which were subjected to oxidation in a "microoxidation" apparatus, in which the absorption of oxygen by the rubber during oxidation could be recorded throughout the induction period.

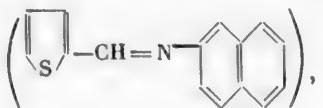
The reference standard was a rubber sample containing phenyl- β -naphthylamine (Neozone D), an antioxidant widely used in the rubber industry.

The kinetic curves for oxidation of rubber in presence of various compounds are given in the figure. The numbers on the curves correspond to the serial numbers of the compounds listed in Tables 1 and 2.

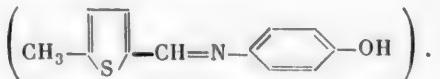
The curve representing the oxidation kinetics of rubber in presence of Neozone D is marked by the number "O". It is clear from the diagram that compounds of serial numbers I-VIII, X, XII, XXII, XXIV, and XXVI have no inhibiting action (the kinetic curves for rubber containing the compounds whose numbers are shown in parentheses are of the same character as those for the other samples listed). A slight inhibiting effect is given by 2-thenylidene- β -naphthylamine (IX), somewhat greater effects are produced by 2-thenylphenylamine (XIX) and 2-thenyl-o-methylphenylamine (XX), while 5-methyl-2-thenylidene-p-aminophenol (XIV), 2-thenyl-p-methoxyphenylamine (XXI), and 2-thenyl- β -naphthylamine (XXIII) are effective inhibitors. The duration of the induction period of rubber oxidation in presence of the last three compounds was not determined because of the great length of the experiments. In their oxidation rates, proportional to the slopes of the linear portions of the kinetic curves, these samples are very similar to rubber containing Neozone D. The best inhibitor of all the compounds tested was 2-thenyl- β -naphthylamine (XXIII).

The following conclusions may be drawn from the results.

1) Azomethine compounds have no inhibiting action. The only exceptions are 2-thenylidene- β -naphthylamine and 5-methyl-2-thenylideneaminophenol, which are very weak inhibitors. Secondary amines are effective inhibitors. These facts are fully consistent with the accepted views on the action mechanism of oxidation inhibitors of the amine and phenol types, according to which oxidation chains are terminated as the result of stabilization of the oxygen-containing polymer radical by a mobile hydrogen atom detached from the inhibitor molecule [17]. Most of the azomethines studied do not contain mobile hydrogen atoms; azomethines which exert some inhibiting action contain either a naphthalene ring with a mobile α hydrogen.



or a phenolic group with a very mobile hydrogen in the OH group

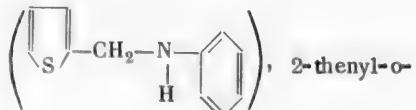


The investigated secondary amines of the thiophene series, like most of the known secondary aromatic amines, have well-defined inhibiting properties due to the presence of mobile amino hydrogen in their molecules.

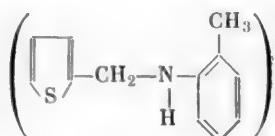
2) Comparison of the inhibiting effects of 2-thenyl- β -naphthylamine and phenyl- β -naphthylamine shows that the influence of the thenyl group ($C_6H_5SCH_2-$) approaches that of the phenyl group.

Comparison of the inhibiting effects of 2-thenylphenylamine and phenyl- β -naphthylamine shows a different result: the positive effect of the naphthalene ring is considerably greater than that of the thenyl group. These results are also consistent with the hypothesis, advanced earlier, that one of the main factors determining the inhibiting action of a compound is the conjugation effect in the molecule [18]. This effect is considerably weaker in the thiophene than in the aromatic derivative.

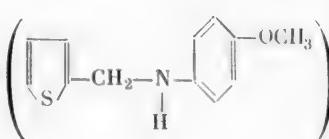
3) Comparison of the inhibiting effects of 2-thenylphenylamine



methylphenylamine



and 2-thenyl-p-methoxyphenylamine



shows that the effectiveness increases sharply in this series. This may be attributed entirely to the effects of substituents present in the ortho- and para positions of the phenyl ring. This fact confirms the relationships established earlier for compounds belonging to the secondary aromatic amines, according to which positive substituents of the first kind, present in the para position in the phenyl ring, increase the inhibiting efficiency of the amines [17].

4) As already stated, the most effective inhibitors of the thiophene derivatives studied are 5-methyl-2-thenyldene-p-aminophenol, 2-thenyl-p-methoxyphenylamine, and 2-thenyl-8-naphthylamine.

Results of Tests of Thiophene Derivatives as Accelerators of Rubber Vulcanization

The synthesized compounds were tested as vulcanization accelerators for SKB, SKS-30, SKN-26 rubbers and natural rubber.

The compounds were introduced into the standard stocks for each type of rubber instead of the accelerators specified in the usual formulations. The mixtures were vulcanized in a press in the form of plates 1 mm thick at 143, 151, and 160°. The quality of each accelerator was characterized by the optimum values of the physical and mechanical characteristics of the rubber in its presence, and by the time required to reach these values.

The results of the experiments showed that six of these thiophene derivatives have the properties of vulcanization accelerators which can be used for curing. These compounds are 2-thenyldeneaminoethanol, 5-methyl-2-thenyldeneaminoethanol, 5-methyl-2-thenyldeneaminophenol, 5-methyl-2-thenyldene-p-anisidine, 2-mercapto-4-(2'-thienyl)thiazole, and bis-2-thenyldeneethylenediamine.

The physical and mechanical characteristics of the rubbers, and the vulcanization conditions in presence of these six compounds, are given in Tables 3, 4, and 5.

TABLE 3
Physical and Mechanical Characteristics of Vulcanizates Based on SKN-26 Rubber

Accelerator	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)
	tion time (min)				tion time (min)			
143°								
Mercaptobenzothiazole	20	115	500	15	20	140	475	10
5-Methyl-2-thenyldene-aminoethanol	60	125	680	40	40	160	630	25
Mercaptobenzothiazole	20	115	500	15	—	—	—	—
5-Methyl-2-thenyldene-p-aminophenol	60	120	770	40	—	—	—	—
Mercaptobenzothiazole	40	280	760	30	—	—	—	—
2-Mercapto-4-(2'-thienyl) thiazole	40	225	660	25	—	—	—	—
151°								

For comparison, characteristics of vulcanizates of the same composition but with mercaptobenzothiazole (Captax) used as accelerator are given in the same tables.

When these results are examined, it will be noticed that of the thiophene derivatives studied the ones to have the properties of accelerators are those having groups characteristic of known accelerators belonging to other classes, such as mercaptobenzothiazole, ethanolamines, and the cross-linking agent p-anisidine.

In a number of publications the mechanism of accelerator action is associated with the ability of a compound to decompose into radicals under vulcanization conditions [19, 20]. The presence of the same groups in

accelerators belonging to different classes, such as $\begin{array}{c} -S \\ \diagdown \\ -N \\ \diagup \\ C-SH \end{array}$ groups in mercaptobenzothiazole and in

2-mercapto-4-(2'-thienyl)thiazole, $=N-C_2H_4OH$ groups in mono-, di-, and triethanolamines, and $=N-C_6H_4OCH_3$ groups in p-anisidine and in 5-methyl-2-thenylidene-p-anisidine, indicates that these groups are responsible for radical formation in the accelerators.

It is also interesting to note that the presence of the methyl group as a substituent in the thiophene ring has a favorable effect on the accelerator action of a compound. For example, if there is no methyl group in position 5 of the thiophene ring the compounds have no accelerating action at all; this is seen if 2-thenylidene-p-anisidine is compared with 5-methyl-2-thenylidene-p-anisidine.

TABLE 4
Physical and Mechanical Characteristics of Vulcanizates Based on Natural Rubber

Accelerator	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)
	tion time (min)				143°			
Mercaptobenzothiazole	20	220	820	12	20	165	750	12
2-Thenylidene-aminoethanol	—	—	—	—	40	165	850	14
5-Methyl-2-thenylidene-aminoethanol	—	—	—	—	40	100	800	15
5-Methyl-2-thenylidene-p-aminophenol	—	—	—	—	60	100	870	18
5-Methyl-2-thenylidene-p-anisidine	—	—	—	—	40	180	850	12
2-Mercapto-4-(2'-thienyl)thiazole	30	110	700	12	—	—	—	—
Di-2-thenylidene-ethylenediamine	35	170	850	15	—	—	—	—

TABLE 5
Physical and Mechanical Characteristics of Vulcanizates Based on SKS-30 and SKB Rubbers

Accelerator	SKS-30				SKB			
	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)	Vulcaniza-	Strength (kg/cm ²)	Relative elongation (%)	Residual elongation (%)
	tion time (min)				tion time (min)			
Mercaptobenzothiazole	20	270	630	20	30	175	550	33
5-Methyl-2-thenylidene-aminoethanol	40	230	700	30	—	—	—	—
5-Methyl-2-thenylidene-p-aminophenol	60	240	715	30	—	—	—	—
5-Methyl-2-thenylidene-p-anisidine	60	220	750	40	—	—	—	—
2-Mercapto-4-(2'-thienyl)thiazole	30	220	510	16	30	115	420	20

Most of the above-named compounds are weaker accelerators than, say, Captax at the ordinary vulcanization temperature (143°). This influences the vulcanization time, increases the residual elongation, and lowers the tensile strength.

However, in a number of cases the difference between the vulcanization times of rubbers containing these substances and Captax respectively decreases with increase of temperature. It is therefore advisable to use these

accelerators for high-temperature vulcanization. In this way, it should be possible to avoid premature vulcanization during preliminary treatment, such as occurs in presence of Captax and other accelerators.

The accelerators in question proved most effective in vulcanization of butadiene-nitrile rubber, and also of butadiene-styrene rubber at high temperatures. The best results were obtained with 2-mercapto-4-(2'-thienyl)thiazole and di-2-thenylideneethylenediamine.

For elucidation of the influence of the thenylidene group on the effectiveness of accelerators, the behavior of thiophene derivatives was compared with that of analogous benzene derivatives: $C_6H_5CH=N-C_6H_4OCH_3$, $C_6H_5CH=NH-C_6H_4OH$, $C_6H_5CH=N-CH_2CH_2OH$.

The results showed that these substances are much weaker accelerators; i.e., presence of the thiophene ring in the molecule has a favorable influence on the accelerating action of a compound.

As already stated, this investigation of thiophene derivatives as ingredients of rubber mixes was confined to studies of their behavior in rubber of one definite formulation. It is likely that by variations of the formulation it might be possible to find conditions in which compounds of this type would prove considerably more effective.

SUMMARY

1. Certain azomethines and secondary amines of the thiophene series were synthesized; it was found that thiophene compounds containing secondary amino or hydroxy groups inhibit the oxidation of rubber.
2. The inhibiting action of these compounds depends to a considerable extent on the nature of ortho and para substituents in the benzene ring.
3. Several of these compounds were found to act as vulcanization accelerators. The most effective are 2-mercapto-4-(2'-thienyl)thiazole and di-2-thenylideneethylenediamine.
4. The thenylidene group has a stronger influence than the benzene ring on the properties of a compound considered as a vulcanization accelerator.

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PREPARATION AND PROPERTIES OF POLYPROPYLENE

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A new class of polymers with a specially regular structure, known in the literature as "isotactic," has recently aroused much interest. One such polymer is polypropylene, first described by Natta [1].

The new crystalline polymeric hydrocarbons have higher melting points, greater densities, and lower solubilities in organic solvents than the corresponding amorphous polymers having the same viscosities in given solvents.

The significance of crystalline polypropylene as a new plastic lies in its ability to form strong films, fibers, and other products. The tensile strength of polypropylene fiber is close to that of steel wire while the density is only one eighth.

The literature contains many communications on the subject of polypropylene, but the polymerization conditions on the pilot or industrial scale are not described. Little is known on methods for characterization of the product.

The present paper contains an account of a method for production of polypropylene in metallic apparatus, and a description of some methods for investigating the properties of technical polypropylene.

EXPERIMENTAL

Polymerization of propylene. Polypropylene was made in presence of catalysts consisting of mixtures of triethylaluminum (AlEt_3) with titanium chlorides (TiCl_4 and TiCl_3) in n-heptane or ligoine (b. p. 90–110°). The concentration of AlEt_3 was varied in the 1–10% range at the molar ratio $\text{AlEt}_3 : \text{TiCl}_n = 1 : 10$ (where $n = 3$ or 4). The experiments were performed in lead-lined, iron, or special-steel reactors, designed to operate at 25 atmos, fitted with anchor-shaped stirrers and immersed in water baths. The autoclave material did not influence the course of the process. Before each experiment oxygen was removed from the reactor by 3-fold evacuation followed by a current of propylene. To charge the autoclave, the required amount of AlEt_3 in its solvent was fed into the autoclave through a siphon in a current of propylene. The required amount of titanium halide was then introduced, the reactor was quickly closed, the stirrer was switched on, and after a definite time liquid propylene was fed in at room temperature. The monomer was supplied from a small cylinder, the amount being found from the weight loss of the latter. The electric heater was then switched on, and the temperature in the reactor was maintained at the required level (40 to 75°, according to conditions).

At the end of the polymerization the gas phase was carefully blown out of the reactor, and the polymer was washed free from catalyst. This was done by addition of methanol into the reactor at the end of the process; the reaction mass was then stirred for one hour at the reaction temperature. The discharged polymer was filtered and washed again with methanol, first slightly acidified with HNO_3 and then pure, until the filtrate became colorless.

Methods for Testing the Properties of Polypropylene

Fractionation of the technical product. A weighed sample of the polymer was sewn in a previously-weighed cloth bag and placed in a round-bottomed flask fitted with a reflux condenser; ether (100 ml per g of polymer) was then added. Fraction I, which was mainly the "amorphous" polymer, was extracted at the boiling point of ether.

The extraction was continued for an hour with periodic shaking, and the extract was then poured off. This extraction was repeated twice more, the amount of ether used being halved. The extracts were combined and concentrated down to 100 ml, and methanol was then added to precipitate Fraction I. The precipitated polymer was filtered off and dried. The polymer remaining in the cloth bag was dried to constant weight and weighed.

The percentage content of Fraction I was determined. A sample of polymer free from Fraction I was taken from the bag, weighed, and extracted with n-heptane at the boil for one hour in a 250 ml round-bottomed flask fitted with a reflux condenser. 100 ml of solvent was taken per g of polymer.

The solution was separated from insoluble polymer on a hot-filtration funnel at 100° through a cloth filter. The residue on the filter was returned to the flask and the extraction was repeated twice more.

The heptane extracts were combined, concentrated down to 100 ml, and acetone was added to precipitate Fraction II, which consisted mainly of the low-molecular crystalline polymer. This polymer was filtered off and dried to constant weight together with the polymer which did not dissolve in either of the solvents used and which was, according to [2], the "isotactic" substance (Fraction III).

The percentage contents of these fractions in the original polymer sample were determined.

Determination of intrinsic viscosity. Viscosity was determined by the usual method [3] in an improved viscosimeter of the capillary type [4] (Fig. 1) at 120°. Determination of the intrinsic viscosity of polypropylene is difficult because of its poor solubility in the known solvents. Therefore, particular attention should be paid to the weights of polymer and solvent taken, and complete solution of the sample should be ensured.

Four solvents were used: decalin, tetralin (at 135°), o-xylene, and chlorobenzene. Determinations in decalin are more accurate because of its greater sensitivity to molecular weight variations of the polymer, but the polymer is more soluble in tetralin (at 135°) and o-xylene.

Fig. 1. Capillary viscosimeter. 1) Viscosimeter body; 2) capillary with two bulbs; 3) air condenser; 4) outlet for diluting the solution; 5) weighing cup; 6) ground-glass stopper.

Density was determined by the free flotation method [5] (at 20°). The liquid used was a mixture of ethyl alcohol and water. The accuracy of the method depends considerably on the method used for preparation of the samples. Satisfactory results were obtained with well-pressed tablets prepared for thermomechanical tests. It is important to avoid the presence of air bubbles within the tablets. This was generally achieved by the following procedure: a sample weighing 0.34 g was put in the mold and tableted at 10 atmos; it was heated to 210°, and the heat was turned off immediately; when the mold cooled to 100° the pressure was raised to 25-30 atmos and the gradual cooling was continued.

Melting points were found from thermomechanical curves determined by means of the Kargin balance.*

RESULTS AND DISCUSSION

When propylene was polymerized in presence of $TiCl_4$, the yield of polymer was 0.5-1.0 kg per liter of reaction solution.

At first the experimental results had poor reproducibility, although all the polymerization conditions were apparently constant. Different polymer batches differed in yield, appearance, and quality. It was later found experimentally that for satisfactory reproducibility the reaction mass must be kept in the reactor at room temperature for 20-30 minutes before the monomer is added. In all probability this time is necessary for formation of the active form of the catalyst.

* Yu. V. Ovchinnikov performed the determinations.

At 5% catalyst concentration and ratio $\text{AlEt}_3 : \text{TiCl}_4 = 5$ (K), the propylene conversion was 90-98%, with 6.8-7.2% consumption of the catalyst. The average molecular weight was 23,000-24,000.

In all cases with $\text{AlEt}_3 + \text{TiCl}_4$ catalysts a mixture of amorphous and crystalline polymer was obtained; the maximum content of polymer with "isotactic" structure did not exceed 45-50% and varied in accordance with the process conditions. The content of amorphous polymer was 25-35%.

TABLE 1
Fractional Composition

Contents of fractions (%)			Melting range (in °C)
I	II	III	
32.3	25.5	42.2	138-154
31.0	19.5	49.5	130-145
30.0	24.0	46.0	135-146
27.0	25.2	47.8	135-155
33.0	23.3	43.7	142-155
33.0	—	—	146-159
33.0	24.9	42.1	144-156

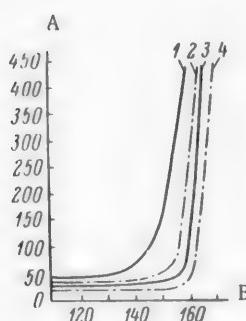


Fig. 2. Thermomechanical test curves. A) Tensile strength (kg/cm^2); B) melting point (in °C); 1) polypropylene prepared in presence of TiCl_4 , 2) Fractions II and III, 3) polypropylene prepared in presence of TiCl_3 , 4) Fraction III.

$\text{AlEt}_3 + \text{TiCl}_3$ catalyst (0.9195) shows that in the second case polypropylene is almost 100% crystalline, whereas if TiCl_4 is used as co-catalyst the polymer is heterogeneous in structure and is a mixture of amorphous and crystalline polymers.

Thus, the degree of crystallinity of the polymer may be found from the density; the relationship is satisfactorily represented by the equation

$$D = 0.92 - 0.00065 A,$$

where D is the density and A is the content (%) of the amorphous fraction in the polymer.

The results of some determinations are summarized in Table 1. The AlEt_3 concentration was 5% at K = 5.

The presence of an amorphous fraction in the technical product under the given process conditions is in all probability characteristic for the system $\text{AlEt}_3 + \text{TiCl}_4$, and it worsens the polymer quality considerably. It follows from the data in Table 1 that the start of the melting range is lowered by 20-25°. The tensile strength also decreases; in the samples tested it did not exceed $200-250 \text{ kg}/\text{cm}^2$. It follows that the properties of the polypropylene samples obtained in our experiments resemble only approximately the properties of the experimental polypropylenes described in [6].

However, the polymer quality can be improved by removal of Fraction I by means of ether. For example, as the amorphous fraction is removed from technical polypropylene the melting range becomes narrower, and in its total absence the polymer melts within 1-2° in the 160-165° range (Fig. 2).

It must be particularly emphasized that when $\text{AlEt}_3 + \text{TiCl}_3$ catalyst is used a crystalline product almost free of amorphous fraction is obtained. In the worst samples of polymer the content of Fraction I did not exceed 5%. The polymer prepared by this method did not differ in properties from the technical polymer made with $\text{AlEt}_3 + \text{TiCl}_4$ catalyst and washed with ether, and in some cases was superior to the latter.

The crystallinity of polypropylene may be characterized by its density. Natta [1] showed that the density of amorphous polypropylene is 0.85, and of crystalline, 0.92.

Our experiments also showed that the density of the amorphous polymer is in the region of 0.855 ± 0.005 , and that of the completely crystalline product is 0.92. It must be stressed that according to our results there was no special density difference between the low-molecular crystalline polymer and the "isotactic" product (Fractions II and III). The density of these samples was in the range of 0.92 ± 0.005 . The results of some determinations are summarized in Table 2.

Comparison of the density of the polymer made with the use of $\text{AlEt}_3 + \text{TiCl}_4$ catalyst (0.89) with the density of the polymer made with $\text{AlEt}_3 + \text{TiCl}_3$ catalyst (0.9195) shows that in the second case polypropylene is almost 100% crystalline, whereas if TiCl_4 is used as co-catalyst the polymer is heterogeneous in structure and is a mixture of amorphous and crystalline polymers.

A particularly detailed study was made of the relationship between the intrinsic viscosity of the polymers, the nature of the solvent, and the fractional composition of polypropylene. The solvents tested were decalin, o-xylene, tetralin, and chlorobenzene.

TABLE 2
Densities of the Polymers Obtained

Contents of fractions (%)			Density	Notes
I	II	III		
100	—	—	0.8622	Amorphous polymer
100	—	—	0.8590	
100	—	—	0.8547	
—	37	63	0.9248	Crystalline polymer
—	—	100	0.9200	
33	24.9	42.1	0.8960	
5	10	85	0.9195	System of AlEt_3 with TiCl_4 System of AlEt_3 with TiCl_3

It was found that solutions of polypropylene in these solvents, at least in the molecular-weight range from 4000 to 120,000, obey the Staudinger equation [7], and that the intrinsic viscosity greatly depends on the nature of the solvent (Fig. 3).

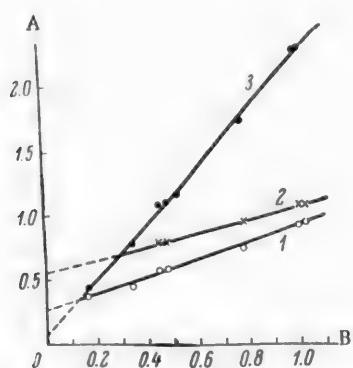


Fig. 3. Variation of the intrinsic viscosity of polypropylene in different solvents with molecular weight. A) Intrinsic viscosity; B) viscosity in tetralin; solvents: 1) o-xylene, 2) chlorobenzene, 3) decalin.

TABLE 3
Molecular Weights of Fractions

Fraction		
I	II	III
8000	13000	92000
17500	42000	113000
16500	41000	—
12500	25000	60000
15500	—	66000
23000	—	118000

From the results presented in Fig. 3, it is easy to derive formulas for conversion of the intrinsic viscosities. Thus,

$$[\eta]_T = 1.6 [\eta]_{OX} - 0.424 = 2.115 [\eta]_{CB} - 1.162 = 0.471 [\eta]_D - 0.0353,$$

where $[\eta]_T$ is the intrinsic viscosity determined in tetralin; $[\eta]_{OX}$ is the intrinsic viscosity in o-xylene; $[\eta]_{CB}$ in chlorobenzene; and $[\eta]_D$, in decalin.

Thus, if the viscosity in one of these solvents is determined, it is easy to calculate the intrinsic viscosity in any of the others.

Since the constant K_M in the Staudinger equation for propylene in tetralin solution at 135° is known ($2.5 \cdot 10^{-5}$ [8]), it follows from the above equations that for polypropylene in o-xylene $K_{OX} = 1.565 \cdot 10^{-5}$, in chlorobenzene $K_{CB} = 1.225 \cdot 10^{-5}$, and in decalin $K_D = 5.33 \cdot 10^{-5}$.

These data were used to determine the molecular weights of different fractions obtained in any given experiment (Table 3).

These results are in full agreement with [8].

SUMMARY

1. The polymerization of propylene in metal autoclaves was studied; it was found that with $\text{AlEt}_3 + \text{TiCl}_4$ catalyst a mixture of amorphous and crystalline polypropylene is obtained; with $\text{AlEt}_3 + \text{TiCl}_3$ mainly the crystalline polymer is formed.

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SYNTHESIS OF DETERGENTS FROM OLEFINS MADE BY HYDROCONDENSATION OF CARBON MONOXIDE WITH ETHYLENE AND PROPYLENE

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It was shown in the preceding paper [1] that hydrocarbons from hydrogenated synthine can be used for production of sodium alkylbenzene sulfonates with surface activity and detergent properties. These substances were synthesized by alkylation of benzene in presence of anhydrous AlCl_3 by means of monochlorides made by chlorination of individual C_7 to C_{17} fractions of hydrogenated synthine, with subsequent sulfonation of the monoalkylbenzenes with oleum.

The purpose of the present investigation was synthesis of sodium alkylbenzene sulfonates from olefins made by catalytic hydrocondensation of carbon monoxide with ethylene and propylene, or by polymerization of the latter in presence of H_2 at low CO concentrations at atmospheric pressure and 190° , with the use of gaseous mixtures of the composition 65–70% C_nH_{2n} , where n is 2 and 3, 25–30% H_2 , and 4–6% CO [2]. The products (hydrocondensates) obtained by these processes resemble synthine in composition, but differ from the latter by having higher olefin contents, which reach about 60% in ethylene hydrocondensate, and about 40% in propylene hydrocondensate.

The hydrocondensates were distilled into fractions corresponding to hydrocarbons from C_6 to C_{17} . These fractions, and also broader fractions (in the case of propylene hydrocondensate) were used for alkylation of benzene by the olefins present in them, in presence of anhydrous aluminum chloride. The monoalkylbenzenes were then converted into sodium alkylbenzene sulfonates. This synthesis does not involve a chlorination stage, such as is necessary in synthesis of alkylbenzene sulfonates from hydrogenated synthine [1]. It is interesting to note that, according to the literature [3], alkylbenzene sulfonates synthesized from synthine olefins made in presence of an iron catalyst at 300 – 400° and 15–40 atmos are superior in surface activity and detergent properties to dodecylbenzene sulfonate made from propylene tetramer.

EXPERIMENTAL

The hydrocondensates were washed three times with 10% NaOH solution and dried over anhydrous copper sulfate. 900 ml of the ethylene hydrocondensate was distilled through a column of 40 theoretical plates up to 120° , and subsequently from a Favorskii flask. Details of the fractions obtained and their physical constants are given in Table 1.

Fractions from C_7 to C_{17} , the olefin contents of which ranged from 76.3 to 29.1%, were used for detergent synthesis. 1400 ml of the propylene hydrocondensate was distilled similarly. Details of the fractions obtained and their physical constants are given in Table 2.

For synthesis of the detergents, combined broad C_{10} to C_{12} and C_{13} to C_{17} fractions were also used, with boiling ranges of 151 – 216° and 216 – 305° and containing 37.0 and 22.3% olefins, respectively.

Alkylation of benzene by the olefins of these fractions was performed as follows. A solution of the hydrocondensate fraction in benzene was added dropwise to a mixture of benzene and anhydrous AlCl_3 heated to 30-35° with stirring. 20 g of AlCl_3 per mole of olefin was taken, and benzene was taken in 10-fold excess, $\frac{1}{5}$ of the total benzene being added with the fraction. The alkylation reaction was continued for 6 hours at 35-55°.

TABLE 1
Fractions from Hydrocondensation of Carbon Monoxide with Ethylene

C_n of fraction	Boiling range (in °C)	Contents in hydrocondensate (vol. %)	n^{20}_{D}	d^{20}_4	Bromine No.	Contents of unsaturated hydrocarbons (%)
C_4	1-4	7.8	—	—	—	—
C_5	20-60	26.0	1.3770	0.6481	185.5	81.2
C_6	60-70	4.0	1.3870	0.6687	158.5	83.1
C_7	70-100	12.9	1.3945	0.6857	146.8	89.5
C_8	100-126	4.9	1.4080	0.7127	108.8	76.3
C_9	126-151	3.6	1.4140	0.7297	82.8	65.4
C_{10}	151-174	6.1	1.4184	0.7357	72.5	64.0
C_{11}	174-200	6.1	1.4240	0.7505	57.8	55.6
C_{12}	200-216	3.7	1.4286	0.7609	47.7	51.2
C_{13}	216-236	3.8	1.4317	0.7686	40.9	46.5
C_{14}	236-250	2.9	1.4350	0.7753	34.1	41.7
C_{15}	250-270	2.9	1.4380	0.7809	27.1	35.6
C_{16}	270-280	1.7	1.4345	0.7825	26.8	37.6
C_{17}	280-303	3.9	1.4420	0.7903	19.6	29.1
Residue	—	9.9	1.4553	—	—	—
Original hydrocondensate	—	100	1.4163	0.7248	91.0	71.8

At the end of the reaction the resin formed was separated off, the reaction mixture was washed consecutively with dilute hydrochloric acid, 5% NaOH solution, and water, and the unchanged benzene was then distilled off. The alkylation product was distilled under vacuum from a Favorskii flask, and the fraction corresponding substantially to monoalkylbenzenes was collected.

TABLE 2
Fractions from Hydrocondensation of Carbon Monoxide with Propylene

C_n of fraction	Boiling range (in °C)	Contents in hydrocondensate (vol. %)	n^{20}_{D}	d^{20}_4	Bromine No.	Contents of unsaturated hydrocarbons (%)
C_{10}	151-174	7.0	1.4175	0.7367	46.1	40.3
C_{11}	174-200	7.6	1.4235	0.7492	38.8	37.3
C_{12}	200-216	4.6	1.4288	0.7587	30.4	31.6
C_{13}	216-236	4.6	1.4322	0.7677	23.6	26.9
C_{14}	236-254	3.4	1.4342	0.7753	19.2	23.6
C_{15}	254-270	2.4	1.4380	0.7811	15.7	20.7
C_{16}	270-280	1.5	1.4400	0.7845	13.2	19.5
C_{17}	280-305	3.8	1.4430	0.7094	11.9	17.8

Data on the monoalkylbenzene fractions are presented in Table 3.

Sulfonation of the monoalkylbenzene fractions was carried out in the same way as the sulfonation of alkylation products from synthine, described earlier [1]. The yield of sodium alkylbenzene sulfonates was 90-100% on

the original alkylation product. The final product was a white or pale yellow powder, and contained 20-40% sulfonates and 80-60% Na_2SO_4 . The surface-active and detergent properties of aqueous solutions of the samples, determined by the methods described earlier [1], are given in Tables 4 and 5.

TABLE 3
Monoalkylbenzenes Prepared from Ethylene and Propylene Hydrocondensates

C_n	ml	Boiling range of monoalkylbenzene fraction		Yield (%) on olefins of C_n fraction)	n^{20}_{D}	d^{20}_4
		(in °C)	pressure (mm)			
C_7	100	206-242	760	32.8	1.4863	0.8572
C_8	28	230-260	760	43.2	1.4883	0.8610
C_{11}	55	115-170	7	56.3	1.4839	0.8546
C_{12}	27	115-175	7	55.2	1.4784	0.8474
C_{13}	28	115-190	7	54.2	1.4726	0.8381
C_{14}	24.5	115-195	7	89.0	1.4645	0.8207
C_{15}	20.5	180-200	7	22.0	1.4760	0.8441
C_{16}	17.5	190-210	7	24.6	1.4770	0.8480
C_{17}	16	180-225	7	54.5	1.4640	0.8234
$C_{10}-C_{12}$	276	130-215	2	30.8	1.4840	0.8623
$C_{13}-C_{17}$	225	130-230	2	~ 100	1.4590	0.8194

It follows from the data in Table 4 that at low pH (in acid media) aqueous solutions of the alkylbenzene sulfonates have no emulsifying power, with the exception of the sample made from the C_{12} fraction of the ethylene hydrocondensate. In this connection, it is interesting to note that alkylbenzene sulfonates made from the corresponding fractions of hydrogenated synthine, from C_{10} upward, have good emulsifying power at low pH [1].

The data in Table 4 show that aqueous solutions of the samples made from ethylene hydrocondensate fractions from C_7 to C_{11} inclusive have high resistance to hard and sea water at 15° at the same pH values.

The resistance to sea water decreases appreciably with increase of molecular weight (lengthening of the side chain). Foaming power first appears in the sample from the C_7 fraction. For solutions of alkylbenzene sulfonates synthesized from fractions C_7 to C_{11} inclusive, the foam has a coarsely cellular and loose structure; foam formed by solutions of samples made from C_{12} and C_{13} fractions has a large volume and a compact microcellular structure. Aqueous solutions of alkylbenzene sulfonates made from C_{15} and higher fractions have a lower tendency to foaming at 20°, and show some increase of foam volume with increase of temperature to 60°.

Table 5 shows that alkylbenzene sulfonates synthesized from broad propylene hydrocondensate fractions form aqueous solutions with good surface-active properties.

Comparison of the properties of these solutions with those of alkylbenzene sulfonates synthesized earlier [1] from corresponding fractions of hydrogenated synthine leads to the conclusion that the product from the broad C_{10} to C_{12} fraction of the propylene hydrocondensate is superior to that from the C_{10} to C_{12} synthine fraction, whereas alkylbenzene sulfonate from the broad C_{13} to C_{17} fraction of the hydrocondensate is inferior to the alkylbenzene sulfonate from the C_{13} to C_{17} synthine fraction.

It should be noted that aqueous solutions of alkylbenzene sulfonates from synthine form foams of better structure — more compact and microcellular — than samples from hydrocondensates. The detergent effect of alkylbenzene sulfonates from broad C_{10} to C_{12} fractions is approximately the same regardless of the starting material, and is somewhat superior to that of ordinary soap [1]. Wool and cotton are washed better than rayon by solutions of these detergents.

TABLE 4
Surface Activity and Detergent Properties of Aqueous Solutions of Alkylbenzene Sulfonates Prepared from Olefins of Ethylene Hydrocondensate

Alkylbenzene	Solution conc. (%)	Solution pH	Wetting power. $\cos \theta$	Emulsifying power	Surface tension (ergs/cm ²)	Resistance to hard water at 15° (ml)	Resistance to sea water at 15° (ml)	Foaming power (ml) at 20°	Foam structure
C ₇	0.5	3.8	0.76473	EUS	30.0	> 100	1% solution	> 100	Loose
	0.25	4.0	0.73610	EUS	37.7	—	—	275/197	
C ₈	0.5	3.8	0.67880	EUS	46.9	—	1% solution	—	Loose
	0.25	3.5	0.81106	EUS	35.9	> 100	1% solution	> 100	
C ₁₁	0.5	3.7	0.76804	EUS	40.9	—	—	270/210	Loose
	0.25	3.9	0.70339	EUS	50.6	—	—	270/210	
C ₁₂	0.5	2.8	0.86340	EUS	30.0	—	1% solution	—	Compact
	0.25	2.9	0.79335	EUS	30.5	> 100	1% solution	> 100	
C ₁₃	0.5	3.1	0.74314	EUS	32.4	—	—	275/195	Compact
	0.25	2.4	0.90946	ES	25.8	—	1% solution	—	
C ₁₅	0.5	2.6	0.83098	ES	29.6	—	—	275/200	Compact
	0.25	2.9	0.78801	ES	31.4	—	—	275/215	
C ₁₆	0.5	4.9	0.90557	separated in 1 hour	25.8	—	1% solution	—	Compact
	0.25	5.2	0.81714	ES	28.6	—	—	275/220	
C ₁₇	0.5	5.5	0.75011	ES	30.7	—	—	275/225	Compact
	0.25	3.0	0.82015	Nil	40.1	—	—	125/75	
C ₁₈	0.5	3.2	0.80073	Separated	43.8	—	—	250/185	Compact
	0.25	3.0	0.75927	Separated	52.3	—	—	160/85	
C ₁₇	0.5	3.7	0.80902	Nil	38.0	—	—	no foam	Compact
	0.25	3.5	0.75492	Separated	41.8	—	—	130/70	
C ₁₈	0.5	3.4	0.68455	Nil	48.5	—	—	140/95	Compact
	0.25	—	0.80366	Separated	49.9	—	—	120/60	
C ₁₇	0.5	—	0.75491	Nil	58.0	—	—	120/60	Compact
	0.25	0.125	0.67816	Separated	65.0	—	—	115/50	

* Emulsion unstable.
** Emulsion stable.

TABLE 5
Surface Activity and Detergent Properties of Aqueous Solutions of Alkylbenzene Sulfonates Prepared from Olefins of Propylene Hydrocondensate

Alkylbenzene sulfonate from fraction of C _n	Solution conc. (%)	Solution pH	Wetting power, cos θ	Surface tension, ergs/cm ²	Emulsifying power	Resistance to hard water (ml)	Foaming power at temp. (in °C)			Detergent effect (%)			
							20		40	60	cotton fabric	wool	rayon
							285/250	290/225	—	268.6	200.0	162.5	
C ₁₀ —C ₁₂	0.5	11.2	0.82577	24.05	ES	—	275/200	280/200	—	290.7	195.5	200.0	
	0.25	10.3	0.77715	25.46	ES	—	275/200	265/200	—	243.8	236.6	181.3	
	0.125	10.1	0.73728	34.85	ES	—	250/200	250/200	—	231.0	144.4	194.0	
	0.06	10.0	0.56280	43.16	ES	—	250/175	250/200	—	215.6	144.4	112.5	
	0.03	9.5	0.45917	50.92	ES	—	120/90	130/110	—	147.0	109.0	119.0	
	0.015	9.5	0.42788	59.21	ES	—	215/165	175/125	275/200	—	—	—	
	0.5	8.2	0.82248	34.85	Nil	1% solution.	215/165	175/125	275/200	—	—	—	
	0.25	8.0	0.79864	34.83	Nil	0.5% solution.	215/160	165/100	275/190	—	—	—	
	0.125	7.5	0.73331	44.03	Nil	8.1	180/130	100/45	195/140	—	—	—	
	0.06	7.0	0.66913	49.21	Nil	—	180/120	Nil	Nil	—	—	—	
C ₁₃ —C ₁₇	0.03	6.8	0.62024	57.04	Separated in 2 hours	—	175/145	Nil	Nil	—	—	—	
	0.015	6.6	0.34202	66.04	—	—	150/90	Nil	Nil	—	—	—	

SUMMARY

1. Olefins in the range of C₇ to C₁₇, made by catalytic hydrocondensation of carbon monoxide with ethylene and propylene, were used for synthesis of sodium alkylbenzene sulfonates, which have the properties of surface-active agents and detergents.
2. The best of the alkylbenzene sulfonates studied were samples made from C₁₁ to C₁₃ fractions of ethylene hydrocondensate, and the broad C₁₀ to C₁₂ fraction of propylene condensate.
3. The surface activity and detergent properties of alkylbenzene sulfonates synthesized from hydrogenated synthine and from the hydrocondensate of carbon monoxide with ethylene and propylene are compared.

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PREPARATION OF QUINOLINE FROM COAL-TAR BASES

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Quinoline is a valuable reagent and raw material for organic synthesis. Pharmaceutical products such as cardiamide, ersetol, chinosol, etc. are made from quinoline. Halogenated alkyl derivatives of quinoline and its homologs are used in the production of cyanine and isocyanine dyes (sensitizers). Quinoline and one of its derivatives (8-hydroxyquinoline) are used as reagents for separation of heavy metals. Being a weakly basic solvent, quinoline is used as a reagent in acylation, esterification, benzoylation, and other reactions. Quinoline has recently become important as a raw material for production of vitamin PP (nicotinic acid) which is also a valuable medicinal product.

Quinoline may either be made synthetically by the Skraup method [1], or isolated from a mixture of coal-tar bases. The Skraup synthesis is unsuitable for production of quinoline on the industrial scale because the reaction proceeds violently and with spattering, the yield is low, and the cost high. Because of this, studies of conditions for isolation of quinoline from coal-tar bases have been performed by many workers in recent years. However, there is very little information in the literature on the subject of isolation of quinoline from coal-tar bases. Apart from certain patents, the only publications are those by Jantzen [2], Schmidt and von Rigen [3], and Krasovitskaya and Nepomnyashchaya [4]. All these workers isolated quinoline by repeated fractional distillation (rectification) of the bases with subsequent repeated crystallization, from alcohol, of sulfates of the bases obtained from narrow fractions. Krasovitskaya and Nepomnyashchaya performed three consecutive rectifications of the original coal-tar bases. The quinoline fraction was converted to the sulfate and repeatedly recrystallized from alcohol, the recrystallized quinoline sulfate was decomposed by alkali, and quinoline was isolated by a final rectification. Jantzen and Schmidt and von Rigen used even more stages. Because of the cumbersome nature of the processes and the low yields, these methods are not used in practice for production of quinoline.

The present paper contains the results of our investigations on the isolation of quinoline from coal-tar bases by high-efficiency rectification.

Coal-tar bases comprise a complex mixture which contains pyridine, aniline, quinoline, isoquinoline, and their methylated homologs; isomeric naphthylamines, and acridine and its derivatives. Over 45 such compounds have been identified to date in coal tar [5]. When coal tar is distilled, the bases present in it are distributed among the different fractions according to their boiling points, and are extracted by means of 20-25% sulfuric acid. Bases are usually extracted from the light-middle and heavy fractions, boiling up to 300°. The bases extracted from these fractions predominantly consist of quinoline, isoquinoline, and their methylated homologs. The quinoline content in these bases, according to different authors, is from 30 to 40% [6, 7].

Coal-tar bases contain 2,3,4,5-tetramethylpyridine (b. p. 233.0°) and isoquinoline (b. p. 243.2°), which are close to quinoline in their boiling points. For isolation of quinoline by rectification it is necessary to separate such pairs of components as 2,3,4,5-tetramethylpyridine and quinoline, with relative volatility 1.144. Calculations and analysis of the separation conditions for these systems show that quinoline may be isolated from coal-tar bases by twofold rectification with a column of efficiency of not less than 25 theoretical plates.

EXPERIMENTAL

Preparation of quinoline under laboratory conditions. The bases were rectified by the following procedure for isolation of quinoline. Rectification of the original bases yielded the following fractions: head fraction, up

to 235°; quinoline fraction, in the 235-240° range; and quinoline-isoquinoline fraction, in the 240-245° range. Rectification of the quinoline fraction gave pure quinoline which distilled over a range of 2.0°, including the boiling point of quinoline, 238.0°. The quinoline contained in the head and quinoline-isoquinoline fractions was obtained from them as a quinoline fraction by rectification.

A sample of coal-tar bases supplied by tar distillers under the name of "heavy pyridine bases" was used for the work. This sample had the following characteristics: d_4^{20} 1.078, water content 3.0%, bases 69.5%, phenols 1.2%; amounts distilled off (in vol. %) were: up to 170°, 3; up to 200°, 7; up to 220°, 42; up to 240°, 62; up to 250°, 78; up to 270°, 88. To remove neutral oils, phenols, and tarry matter, the original bases were treated with 25% sulfuric acid. The base sulfates formed were washed twice with xylene. The purified sulfates were decomposed by 20% caustic soda. The purified bases had the following characteristics: d_4^{20} 1.067, water 1.0%, bases 98.8%, phenols absent; amounts distilled off (in vol. %) were: up to 170°, 6; up to 200°, 8; up to 230°, 39; up to 240°, 61; up to 250°, 77; and up to 270°, 84.

The purified bases were rectified with the aid of a column consisting of a brass tube 30-32 mm in diameter and 2160 mm long. The column was packed with single-turn spirals 5 mm in diameter made from copper wire 0.5 mm thick. The specific surface of this packing is $9.65 \text{ cm}^2/\text{cm}^3$. The packing height was 2000 mm, and the total area of the packing in the column was 1.35 m^2 . The column efficiency (for a mixture of benzene and carbon tetrachloride) was 28 theoretical plates. To maintain adiabatic conditions, the column was equipped with variable electric heating and thoroughly lagged. The boiling ranges of fractions collected at reflux ratio 6-7 were: head, 115.0-236.0°; quinoline, 236.2-240.1°; quinoline-isoquinoline, 239.6-244.5°. The yields of the fractions (in wt. %) were: head, 43.7-46.9; quinoline, 15.8-18.6; quinoline-isoquinoline, 7.8-10.5.

The quinoline fraction was rectified with the aid of the column described above, for isolation of quinoline. The distillate was collected in one-degree steps at reflux ratio from 8 to 10. The rectification products collected up to 235.5° boiled in the 222.6-235.5° range, and were virtually free from quinoline. The boiling range suggests that they consist mainly of isomeric xylidines and 2,3,4,5-tetramethylpyridine [5]. The products collected in the 235.5-237.5° range comprise the quinoline fraction, which distills in the 233.9-238.3° range. The distillate following the quinoline fraction, collected in the 237.5-239.5° range, consists of quinoline which distills in the 237.7-239.1° range. The characteristics and evaluation of this quinoline are given in greater detail below. The last distillates from the quinoline fraction, collected up to 242.5°, distill in the range between the boiling points of quinoline and isoquinoline.

The total yields of the rectification products obtained from the quinoline fraction are given below.

	Yield on quinoline fraction (%)	Yield on original bases (%)
Fraction of methylated pyridine and aniline homologs	14.0	2.5
Quinoline fraction	11.0	1.9
Quinoline	58.3	10.3
Quinoline-isoquinoline fraction	12.4	2.2

In addition to the quinoline fraction, its adjacent head and quinoline-isoquinoline fractions were rectified. The column described above was used. The head fraction was rectified at reflux ratio 8-10, and the quinoline-isoquinoline fraction, at 10-13.

The total yields of the rectification products obtained from the head fraction are given below.

	Yield on head fraction (%)	Yield on original bases (%)
Fraction of methylated pyridine and aniline homologs, distilling up to 233.7°	71.7	32.5
Head fraction, distilling in the 228.6 to 236.7° range	11.8	5.4
Quinoline fraction, distilling in the 235.7-238.7° range	13.6	6.2

TABLE I
Industrial Trials of Quinoline Production

Material distilled	Yields and characteristics of fractions																
	Light distillates			head			quinoline fraction			quinoline-isoquinoline fraction			quinoline				
	yield (wt.%)	d_{4}^{20}	s.b. •	e.b. •		yield (wt.%)	d_{4}^{20}	s.b. •	e.b. •	yield (wt.%)	d_{4}^{20}	s.b. •	e.b. •	yield (wt.%)	d_{4}^{20}	s.b. •	e.b. •
Heavy pyridine bases	13.7	1.051	224.0	238.7	22.2	236.9	241.9	14.7	1.071	240.0	247.9	—	—	—	—	—	—
Head fraction	13.7	—	—	—	30.7	236.2	239.7	—	—	—	—	—	—	—	—	—	—
Quinoline fraction	19.6	—	—	—	8.5	236.7	239.8	—	—	—	—	—	—	—	—	—	—
Quinoline-isoquinoline fraction	—	—	—	—	40.0	—	237.2	240.4	31.9	—	—	—	—	—	—	—	—

• s. b. = start of boiling. e. b. = end of boiling (in °C). Temperatures corrected for atmospheric pressure.

Rectification of the quinoline-isoquinoline fraction yielded 52.2% of quinoline fraction (4.7% on the original bases) distilling in the 235.6-240.9° range.

The total quinoline yield was 18.5% on the original bases. The yield of the quinoline fraction was 17.6% in the primary rectification and 13.9% in the secondary rectifications.

Production of quinoline under industrial conditions. The results of the laboratory experiments were checked on the industrial scale in a pilot unit with a packed column filled with single-coil spirals of 10 mm inside diameter, made from iron wire 1.0 mm thick. This packing has the following characteristics: bulk density 1396 kg/m³, specific surface 668 m²/m³, free volume 85%. The packing was arranged in six layers each 950 mm high, and 50 mm apart.

Bases isolated from the absorption fraction of coal tar were used as the starting material for production of quinoline. These bases had the following characteristics: d_{4}^{20} 1.083, water content 10.6%, bases 82.2%; boiling range: start, 234°; 20%, 242°; 50%, 249°; 80%, 258°; and 90%, 295°. In contrast to the laboratory experiments, the bases were not treated for removal of neutral oils and tarry matter. As in the laboratory experiments, the following fractions were collected: head, up to 235°; quinoline, in the 235-240° range; and quinoline-isoquinoline, in the 240-245° range. The reflux ratios were from 6.8 to 8.0.

The fractions were collected at the temperatures (corrected) of the vapors leaving the column. The distillate collected up to 200° consisted mainly of water, with a small amount of light distillates.

The fractions obtained in primary rectification of the bases were subjected to repeated rectification. Quinoline was isolated from the quinoline fraction at reflux ratio 9-10. In addition to quinoline, the following fractions were isolated: head, up to 235°; quinoline fraction, from 235-239°, and quinoline-isoquinoline fraction, 239-245°.

In rectification of the quinoline-isoquinoline fraction (at reflux ratio 8-9), the concentrated quinoline fraction boiling in the 237-240° range was collected. The yields and characteristics of the rectification products obtained from heavy pyridine bases and the head, quinoline, and quinoline-isoquinoline fractions are given in Table 1.

It is clear from these results that the pilot-plant experiments confirmed that quinoline can be isolated from coal-tar bases by rectification. The total quinoline yield from the original (100%) bases was 21-22%, i.e., 3% higher than in the laboratory experiments.

Owing to the absence of appropriate analytical methods it is difficult to estimate the content of quinoline in the product. Polarographic estimation of quinoline does not give satisfactory results with a highly concentrated product, as the accuracy of the method does not exceed $\pm 5\%$ (relative) [8].

According to [9], quinoline which boils over a range of 2.0° including the boiling point of quinoline contains 95% of the base. Since the boiling range is insufficient for evaluation of the quinoline, the melting points of the sulfate and picrate were also determined. These values were compared with the values obtained for quinoline synthesized by the Skraup method. In addition, the yields of nicotinic acid, obtained by catalytic oxidation with sulfuric acid, from synthetic quinoline and from quinoline isolated from coal-tar bases were compared [10]. The results (Table 2) show that quinoline isolated from the bases by rectification differs hardly at all from synthetic quinoline. It is a fully satisfactory raw material for production of nicotinic acid and for other syntheses.

TABLE 2
Comparison of Quinolines

Characteristics	Synthetic quinoline		Quinoline isolated from bases	
Boiling range of d_{5}^{20} 95% (in $^\circ C$)		1.0933		1.0929
Melting point of acid sulfate (in $^\circ C$)		1.4		1.5-2.0
		164.1		164.0
Melting point of picrate (in $^\circ C$)		202.3		201.8
Yield of nicotinic acid on oxidation:	Expt. No. 1	Expt. No. 2	Expt. No. 1	Expt. No. 2
quinoline taken for oxidation (g)	25.8	25.8	20.0	20.0
nicotinic acid obtained (g)	12.3	11.7	9.3	9.4
yield on quinoline (%)	47.6	45.3	46.5	47.0
yield, % of theoretical melting point (in $^\circ C$)	50.0 230-232	47.7 230-231	48.6 230-231	49.0 230

Isoquinoline is the main impurity in technical quinoline obtained from coal-tar bases by rectification. We showed earlier [11, 12] that the solubility of acid quinoline sulfate in ethyl alcohol is considerably higher than that of acid isoquinoline sulfate. This fact was used to isolate pure quinoline of the following characteristics from technical quinoline: d_{4}^{20} 1.0932, boiling range $237.5-238.7^\circ$, n_{D}^{20} 1.6261, melting point of acid sulfate 163.2° .

SUMMARY

1. Technical quinoline was isolated by a new method from coal-tar bases; it boils over a 2° range including the boiling point of pure quinoline (238.0°), and is close in its properties to synthetic quinoline.
2. Pure quinoline was prepared from technical quinoline by removal of isoquinoline (as the acid sulfate).

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USE OF β -CHLORO ETHERS MIXED WITH DICHLORIDES FOR DEPARAFFINIZATION OF AVIATION OIL

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Removal of solid paraffins (deparaffinization) is an important problem in oil production technology. Selective solvents are widely used, both in our oil industry and abroad, for production of low-temperature lubricating oils from paraffin-containing crudes by deparaffinization [1, 2].

The commonest method for oil deparaffinization is the benzene-ketone method. The solvents used in refinery practice are mixtures containing 25-50% methyl ethyl ketone, 12-25% toluene, and 40-60% benzene. Mixtures of normal ketones: methyl propyl ketone and methyl butyl ketone, are used as selective solvents [3]. Methyl Isobutyl ketone can also be used as an individual selective solvent [4].

A mixture of dichloroethane and benzene is used in refinery practice for deparaffinization of oils. The mixture consists of 22-25% benzene and 78-75% dichloroethane. An advantage of this over the benzene-ketone method is the low temperature gradient, 5-10°, of deparaffinization. Disadvantages of the method are: a high yield of petrolatum, toxicity of dichloroethane, and corrosion of the equipment when dichloroethane decomposes during distillation if it is heated above 140°.

Various chlorinated hydrocarbons [5] and their mixtures with each other or with substances of other types have been recommended for oil deparaffinization.

The β -chloro ethers are also of interest as solvents. In many instances they are more valuable solvents than other chlorinated compounds [6]. Chemically, β -chloro ethers are fairly stable compounds, they are fairly resistant to the action of caustic alkali, are difficultly hydrolyzed by water on heating, and are of low toxicity. They are good solvents for many organic substances and mineral salts. Because of the stability of β -chloro ethers (the chlorine is difficult to split off), they can be recommended as noncorrosive solvents, new extracting agents, selective solvents for purification of lubricating oils, etc. The time is now ripe to develop an industrial process for synthesis of β -chloro ethers from olefins of petroleum cracking fractions. Systematic investigations are in progress [7-12] on the synthesis of β -chloro ethers from olefins made by cracking, and on the utilization of β -chloro ethers mixed with dichlorides as solvents for deparaffinization of aviation oils. Certain β -chloro ethers mixed with dichlorides, when used as solvents for deparaffinization of aviation oils, extracted over 70% of oil with pour points of -18° and lower from the crude materials [8, 11, 12].

The purpose of the present investigation was to test, as solvents for deparaffinization of aviation oil, β -chloroethyl methyl and β -chloroethyl ethers (synthesized from ethylene) mixed with dichloroethane [10].

EXPERIMENTAL

The following solvents, composed of dichloride and β -chloro ethers, were tested for deparaffinization of aviation oil:

Composition of solvent (%)	Temperature (in ° C)	d_{4}^{20}	n_{D}^{20}
85 of β -chloromethyl ether + + 15 of dichloroethane	87- 94	1.1092	1.4167
82.3 of β -chloroethyl ether + + 17.7 of dichloroethane	100-109	1.0417	1.4168
69.2 of β -chloroethyl ether + + 30.8 of dichloroethane	82-109	1.0615	1.4210
53.3 of β -chloroethyl ether + + 46.7 of dichloroethane	82-109	1.117	1.4247

For deparaffinization of aviation oil a raffinate made from crude Karachukhur-Surakhany heavy oil was used, of the following characteristics: d_{4}^{20} 0.882, kinematic viscosity at 100° (centistokes) 20.4, viscosity-weight constant 0.803, coke value 0.214%, Pensky Martin flash point 217°, NPA color 7.

The mixture of raffinate and solvent was warmed to 60° to dissolve the raffinate, cooled to the required temperature in a refrigerator, and filtered. A raffinate - solvent ratio of 1:4 was maintained in the experiments. The solvent was distilled from the filtrate under vacuum, and the constants of the oil were then determined. The results are summarized in the table.

Results of Solvent Deparaffinization of Aviation Oil, and Properties of the Oils Obtained

Expt. No.	Solvent	Temp. (in ° C)	Deparaffinization temp. (in ° C)	Solidification temp. of de-paraffinized oil (in ° C)	d_{4}^{20}	Kinematic viscosity at 100° (centistokes)	Ratio of kinematic viscosities at 50° and 100°	Viscosity index
				Yield of oil (%)				
1	85% β -chloroethyl methyl ether + 15% dichloroethane	87-94	-20	Below -25	18.7	0.890	19.05	7.86
2	74.4% of solvent of Expt. 1 + 26.6% benzene	87-94	-20	-19	63.4	0.896	20.82	7.76
3	82.3% β -chloroethyl ether + 17.7% dichloroethane	100-109	-20	-19	50.0	0.896	20.4	7.63
4	69.2% β -chloroethyl ether + 30.8% dichloroethane	82-109	-20	-22	40.0	0.898	20.15	7.68
5	The same	the same	-15	-17	52.11	0.896	20.6	7.58
6	53.3% β -chloroethyl ether + 46.7% dichloroethane	82-109	-15	-18	38.2	0.897	17.82	7.25
7	The same	the same	-10	-12	54.6	0.894	20.42	7.44
8	Dichloroethane -- benzene (works solvent)	—	-25	-19	73.2	0.894	20.20	7.70

It follows from the data in the table that the solvent consisting of 85% chloro ether and 15% dichloride (Experiment 1) has insufficient solvent power for the oil components, so that a large amount of oil is deposited at low temperatures with the paraffins.

The yield of oil was higher in Experiment 2, with the use of a mixture consisting of 74.4% of the solvent used in Experiment 1 and 26.6% benzene. It is noteworthy that the solidification temperature of the oil obtained is almost the same as the deparaffinization temperature, which is an advantage.

As is known, in deparaffinization practice benzene (22-25%) is added to dichloroethane in order to increase the yield of deparaffinized oil.

The solvent used in Experiment 3, consisting of 82.3% chloro ether and 17.7% dichloride, extracted more oil (50%) from the crude than the solvent used in Experiment 1. The solvents used in Experiments 3 and 1 contained almost the same percentage of chloro ethers; the ethyl radical in the alkoxy group of β -chloroethyl ether may have caused the higher yield of oil in Experiment 3. It is likely that increase of the number of carbon atoms in the alkoxy group should increase the oil yield further.

The solvent in Experiment 4, consisting of 69.2% chloro ether and 30.8% dichloride, extracted somewhat less oil (40%) from the crude than the solvent in Experiment 3, but the temperature gradient of deparaffinization was positive.

The difference between the deparaffinization temperature and the solidification temperature of the deparaffinized oil determines the so-called temperature gradient of deparaffinization.

The solvent used in Experiment 5, the same as in Experiment 4, extracted rather more oil (52.11%) from the crude at deparaffinization temperature -15° ; the solidification temperature was -17° . The temperature gradient of deparaffinization was positive.

The solvent in Experiment 6, consisting of 53.3% chloro ether and 46.7% dichloride, extracted rather less oil (38.2%) at the same deparaffinization temperature as in Experiment 5; the solidification temperature of the oil was -18° . The temperature gradient of deparaffinization was positive again.

A positive temperature gradient of deparaffinization was also found in Experiment 7, where the same solvent as in Experiment 6 was used. The deparaffinization was performed at -10° , and the oil yield was 54.6%; the solidification temperature was -12° .

In industrial practice solvent deparaffinization of oils is carried out at -25° and lower, and the oil obtained has a solidification temperature of -18° and lower, so that the temperature gradient of deparaffinization is negative.

It is seen in the table that in Experiments 1, 4-7, the temperature gradient of deparaffinization is positive.

SUMMARY

1. It is shown that a mixture of β -chloroethyl methyl ether and dichloroethane (Experiment 1) has the lowest solvent power for the oil components of low temperatures.

2. A mixture of β -chloroethyl ether and dichloroethane dissolves more oil components at low temperatures than the above-named mixture.

3. A distinctive feature of the deparaffinization solvents tested, consisting of β -chloro ethers and dichlorides, is the absence of a temperature gradient of deparaffinization, or even the presence of a positive temperature gradient, which is highly desirable in deparaffinization of lubricating oils.

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BRIEF COMMUNICATIONS

EFFECT OF IRON SALTS ON WATERPROOFING OF SOILS*

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It is known that soils are highly hydrophilic and if they are to be used for road construction they must be made water-resistant and have adequate mechanical strength under moist conditions. This is achieved by treatment of soils with bitumens and tars. However, the necessary waterproofness is not attained in this manner. It has been shown in a number of investigations [1, 2] that the hydrophilic properties of soils are diminished considerably by the action of trivalent cations. According to Antipov-Karataev [3], soils may be strengthened by "cementing" of the aggregates by ferric hydroxide, either adsorbed on adjacent particles or filling the pores between them. Fuks also refers to stable structures of soil suspensions, in which the particles are bonded by means of iron humates [4].

Moreover, iron salts have a favorable influence on the colloidal properties of soils, as shown in their interaction with the surface-active components of bitumens — asphaltogenic acids. Similar processes were studied by Kolyasev and Lysenko [5].

Ferric cations enter the inner micellar layers and displace univalent ions. The micelles thereby undergo charge reversal, and the diffuse layer now consists of anions which can be exchanged for surface-active anions; in this instance, asphaltogenic acid anions. Moreover, the considerable increase of soil acidity under the influence of iron salts also favors dissociation of amphotytic compounds in the soil in the alkaline direction, and this also assists adsorption of anions from the surface-active substances in bitumens and tars by the soil sorption complex.

It is also to be expected that iron salts enter into chemisorptive interaction with the acid components of bitumens and tars, forming water-insoluble iron phenolates and asphaltogenates. All these data indicate that iron salts should intensify hydrophobization of soils treated by bitumens and tars. We carried out investigations in this connection, with the use of ferrous and ferric sulfates and ferric chloride.

EXPERIMENTAL

The material used for the study was the humus layer of chernozem from the Kiev region, taken from a depth of 0-20 cm, of the dusty loam type. This soil was treated either with B-3 petroleum bitumen, or D-2 crude coal tar. Some of the samples were treated with iron salts before being mixed with the bitumen or tar. The procedure was as follows: the soil was dried to the air-dry state, ground in a roll mill, and sifted. The calculated amount of iron salt in solution form was added to this soil, and the whole was thoroughly mixed. The amount of water added was close to the maximum molecular moisture capacity of the soil. The mixtures were kept for 24 hours in a desiccator over water, bitumen or tar heated to 70-90° was added, and the whole mass was stirred thoroughly again until homogeneous. Some of the mixtures did not contain added iron salts. The mixtures were molded into specimens (5 × 5 cm) in a hydraulic press under a static load of 300 kg/cm². The molded specimens were kept in a thermostat at 16-22° for 7 days or 3 months.

For estimation of the waterproofing effect of iron salts the 7-day and 3-month specimens were saturated with water, and the water absorption and compressive strength were then determined. The water saturation was performed as follows: the specimens were kept for 1 hour in water, then for 1.5 hours under vacuum (residual pressure, 15-20 mm), and then again for 2.5 hours in water.

* Work performed under the guidance of K. A. Knyazyuk.

The results of the experiments are given in Tables 1 and 2.

TABLE 1

Properties of Soil Specimens Treated with Iron Salts and Bitumen

Specimen No.	Addition to soil	7-day specimens		3-month specimens	
		water absorption (% by wt.)	compressive strength of saturated specimens (kg/cm ²)	water absorption (% by wt.)	compressive strength of saturated specimens (kg/cm ²)
1	No additions	Destroyed		Destroyed (quite intact without vacuum)	
2	0.5% FeCl ₃				
3	1% FeCl ₃				
4	2% FeCl ₃	Destroyed (unbroken without vacuum, edges damaged)	0		
5	3.5% bitumen	Destroyed	0	Partially destroyed	4.2
6	7% bitumen	9.1	2.8	6.4	4.5
7	3.5% bitumen + 2% FeSO ₄	3.2	8.2	5.1	12.2
8	3.5% bitumen + 2% Fe ₂ (SO ₄) ₃	3.4	7.2	5.8	8.2
9	3.5% bitumen + 2% FeCl ₃	Partially destroyed	3.3	4.8	6.4

It follows from the data in Table 1 that addition of 2% ferric chloride waterproofs soil appreciably, and if saturated without use of vacuum the specimens proved resistant (Specimen No. 4), whereas Specimens Nos. 1, 2, and 3, not treated with ferric chloride or containing less than 2% of it, were converted into a shapeless mass under these saturation conditions. However, ferric chloride by itself cannot confer the necessary water resistance to this soil, and has this effect only in conjunction with bitumen. It is interesting to note that bitumen alone, when 3.5% is used, exerts a waterproofing effect only after some time, as is seen in the results for Specimen No. 5. Even 7% of bitumen after 3 months of exposure does not increase the mechanical strength sufficiently in the water-saturated state (Specimen No. 6). Combined treatment with 3.5% of bitumen and 2% of iron salts

TABLE 2

Properties of Soil Specimens Treated with Iron Salts and Tar

Specimen No.	Addition to soil	7-day specimens		3-month specimens	
		water absorption (% by wt.)	compressive strength of saturated specimens (kg/cm ²)	water absorption (% by wt.)	compressive strength of saturated specimens (kg/cm ²)
1	No additions	Destroyed		Destroyed	
2	3.5% tar	Partially destroyed	4.2	8.2	6.7
3	3.5% tar + 0.5% FeSO ₄	4.2	8.3	6.1	9.6
4	3.5% tar + 0.5% Fe ₂ (SO ₄) ₃	4.5	6.7	7.1	8.6
5	3.5% tar + 0.5% FeCl ₃	4.8	6.1	6.5	9.6
6	3.5% tar + 1% FeCl ₃	3.5	8.6	6.6	10.4
7	7% tar	4.7	5.1	9.2	10.0
8	7% tar + 0.5% FeSO ₄	3.9	9.5	6.5	12.5
9	7% tar + 0.5% FeCl ₃	2.9	9.6	6.5	16.0
10	7% tar + 1% FeCl ₃	4.5	10.1	5.7	20.0

proves effective with the use of iron sulfates (Specimens Nos. 8 and 9), and is more effective than the use of bitumen alone (compare Specimens Nos. 7, 8, 9, and 5). It is interesting that addition of 2% of ferrous sulfate is so effective that it gives a better waterproofing effect, especially in relation to compressive strength, than a two-fold increase of the bitumen content. The tables show that the action of iron salts intensifies with time.

It follows from Table 2 that in tar treatment iron salts have a similar effect, decreasing the tendency of the soil to adsorb water and conferring a greater mechanical strength on it in the water-saturated state in comparison with the action of tar alone (compare specimens Nos. 3, 4, 5, 6, with No. 2); the most effective addition was 1% FeCl_3 , especially in conjunction with 7% of tar (Specimens Nos. 9 and 10). These results are of practical significance, as they indicate that less bitumen need be used if iron salts are added, and when tar is used for waterproofing the effect is increased considerably by small additions of iron salts. Since iron sulfates and chlorides are waste products of metallurgical and bromine plants, these data show that further investigations and practical applications of iron salts as waterproofing additives in treatment of soils with organic binders are desirable.

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THE ROLE OF MASS TRANSFER BETWEEN GAS AND LIQUID IN CHLORINATION OF A MAGNESIUM OXIDE SUSPENSION IN A CHLORIDE MELT

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In recent years the production of anhydrous metal chlorides by chlorination of their oxides has been extensively practised in industry. This paper is concerned with a variation of this method, discussed little in the literature, consisting of chlorination of oxides suspended in a salt melt in a plate bubble tower.

Synthetic carnallite of factory origin, the composition of which after it had been heated at 700° for 30 minutes is given in Table 1, was used for chlorination. The content of residual water of constitution was not determined, but from earlier work [1] it is known to be about 0.15%.

The reducing agent was coke, size - 100 to + 140 mesh, containing 3.79% moisture, 80.33% carbon, and 11.66% ash. The amount of coke was in 50% excess over the amount calculated from the equation $\text{MgO} + \text{C} + \text{Cl}_2 = \text{MgCl}_2 + \text{CO}$. The amount of chlorine used, also taken in 50% excess, was calculated from the same equation. Technical chlorine (from a steel cylinder) was used.

The chlorinators were made from quartz glass, in the form of tubes 42 mm in diameter and 250 mm long, in which flat plates with 9 holes 4 mm in diameter were sealed; 1, 2 (40 mm apart) or 4 (20 mm apart) plates were used. Chlorine was introduced from below through a tube 7 mm in diameter.

A charge consisting of 200 g of carnallite and the necessary amount of coke was put in the chlorinator heated to 700°, placed in a vertical electric furnace together with the gas inlet tube. The chlorinator was closed by a bung with an outlet tube and a thermocouple sheath, and a water-jet pump was then turned on for drawing the gases through. After a temperature of 700° had been reached, a mixture of chlorine and air (dried over sulfuric acid) in the required proportions was passed in; this was noted as the start of the experiment. The temperature was maintained at 700 ± 10° by regulation of the current. The gas feed rate was regulated by means of valves and measured by rheometers. At the end of a fixed time the gas supply was stopped, the melt was poured into a stainless-steel basin, cooled and weighed; a sample was then taken for analysis.

The MgO content was determined by alkalimetric titration. The magnesium ion content in aqueous solution was determined by titration with Trilon B with chromogen dark blue indicator, and calculated as $MgCl_2$.

TABLE 1
Chemical Composition of Two Carnallite
Samples (in %)

Carnallite	MgO	$MgCl_2$	Cl^-	Fe_2O_3	H_2O
A	5.70	45.55	55.61	0.02	(0.15)
B	4.01	47.20	58.30	0.02	(0.15)

The experiments were performed in series; in each series the number of plates in the chlorinator was varied but the other conditions were maintained constant. A total of 8 series was conducted; the series numbers are given in Table 2 and Figs. 1 and 2 (the numbers on the curves correspond to the series numbers).

Table 2 gives the volume velocity v at 700° of the gaseous mixture entering the chlorinator, the Cl_2 content of this mixture (%), the total volume V (in liters reduced to standard conditions) of chlorine supplied during the experiment, and the chlorination time (t) in each experiment.

The amount of magnesium oxide converted (m) was calculated from the change in the $MgCl_2$ content of the melt during the experiment.

To determine the chlorination rate, the average amount of magnesium oxide (in g) converted per minute into $MgCl_2$ was divided by the weight-average fraction of MgO during the experiment:

$$w = \frac{m}{t \cdot (\% \text{MgO} : 100)} .$$

Expression of the rate in this form made it possible to compare chlorination rates in different experiments, in which the carnallite composition or the degree of chlorination were different.

Chlorine conversion was calculated from the ratio of the amount of magnesium oxide converted to the initial amount in suspension, with a correction for excess chlorine:

$$\eta = \frac{m}{1.5m_{\text{initial}}} .$$

It is clear that with complete conversion of MgO into $MgCl_2$, $\eta = 0.67$.

TABLE 2
Experimental Conditions

Exptl series	Cl_2 (%)	t (min)	v (cm ³ /sec)	v (corr. liters)
1	70	30	18.1	6.42
2	20	30	63.2	6.42
3	100	30	12.6	6.42
4	40	30	31.6	6.42
5	40	50	19.1	6.42
6	40	75	12.6	6.42
7	20	150	16.5 *and 12.5	8.33 *and 6.42
8	70	43	16.5 *and 12.6	8.33 *and 6.42

* The larger values refer to carnallite A and a chlorinator with one plate.

It is clear from the relative positions of Curves 3, 8, 6, and 7 in Fig. 1 that the chlorination rate increases with increase of chlorine concentration in the gas mixture. This also follows from the relative positions of Curves 1 and 5. This relationship suggests that absorption of chlorine by the chloride melt plays a significant role in the mechanism of this process, as the driving force of absorption should increase with the partial pressure of chlorine. The possibility of absorption in this system is confirmed by the real if low solubility of chlorine in fused carnallite; according to our determinations, it is $10^{-3}\%$ at 610° and 1 atmos partial pressure of chlorine.

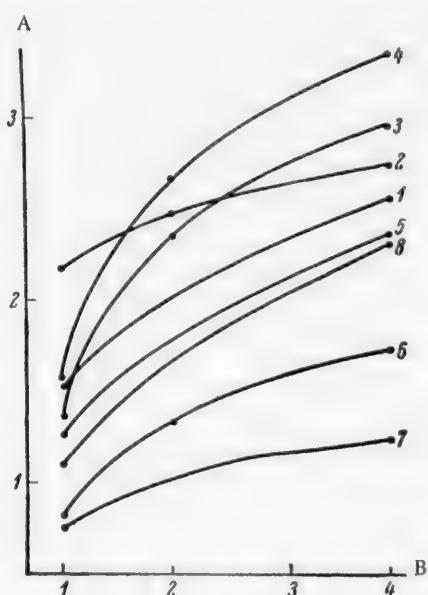


Fig. 1. Chlorination rate. A) Chlorination rate (w); B) number of plates in chlorinator.

It also follows from a comparison of the same curves in Fig. 2 that the conversion of chlorine increases with decrease of the chlorine concentration in the gas phase. On the assumption that chlorine is absorbed by

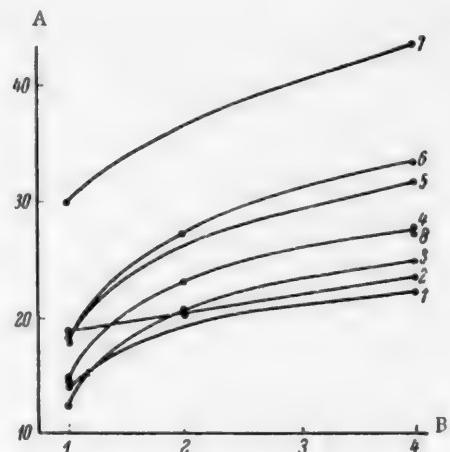


Fig. 2. Chlorine conversion. A) Chlorine conversion η ; B) number of plates in chlorinator.

the melt, the explanation for this relationship is that as the chlorine becomes more diluted with air the total absorption surface in the experiment increases; in other words, the specific interfacial area per unit weight of chlorine increases.

The ascent of all the curves in Figs. 1 and 2 indicates that increase of the number of plates has a favorable effect; this is consistent with the general mass-transfer relationships in plate columns. The curves in Figs. 1 and 2 tend to flatten with increase of the number of plates, since the addition of each consecutive plate produces a diminishing effect. The useful role of the plates may be attributed to the influence of the number of plates on the extent of the bubbling surface in the plate chlorinator. At the gas rates used continuous foam was not formed on the melt surface, but the bubbles persisted for some time under each plate and sometimes coalesced there into "gas cushions." The plates increased gasification of the melt and therefore the gas-liquid contact area.

In explaining the influence of the number of plates even more importance should be attached to the formation of a new interface as the gas passes through each orifice in the plates; this was noted in studies of bubbling in other physicochemical systems. For example, it was noted in a study of the absorption of nitrogen oxides by alkaline solutions and milk of lime [2] that the first layer of solution, adjacent to the gas inlet, is much more effective than the rest of the liquid layer. This was termed the entry effect, and was attributed to renewal of the liquid film. In absorption of chlorine, which has low solubility in the chloride melt, renewal of the liquid film which represents the main resistance should be of great importance.

In the chlorination process in question, bilateral mass transfer takes place: absorption of chlorine and desorption of carbon oxides. The literature contains a paper [3] in which the significance of the entry effect is also demonstrated for transfer from the liquid to the gas phase. Calderbank, who studied the desorption of oxygen from water by means of air on a sieve plate, concluded that the mass-transfer conditions during formation and growth of the bubbles largely determine plate efficiency.

From a comparison of Curves 6, 5, and 4 in Fig. 1 it follows that the chlorination rate increases with increase of the gas velocity. The same follows from Curves 7 and 3, and 8 and 1, respectively. Turbulence of the melt, which increases with increase of the gas rate, evidently plays a role here. Turbulence should favor subdivision of the bubbles, improve the homogeneity of the suspension, and lower diffusion resistance. However, the conversion of chlorine decreases with increase of gas velocity, as is clear from the positions of the curves in Fig. 2.

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INVESTIGATION OF THE CONDITIONS FOR PRECIPITATION OF COPPER - GERMANIUM SULFIDE OF THE TYPE $\text{CuS} \cdot \text{GeS}_2$, WITH THE AID OF RADIOACTIVE GERMANIUM

V. I. Davydov and N. P. Diev

Natural germanium minerals such as germanite and renierite are complex sulfides of germanium and copper, iron, and other metals [1-3]. In some complex sulfide ores germanium is present in the form of inclusions of the above-named minerals [4, 5]. Therefore, it is necessary to study and to prepare the double copper-germanium sulfide in order to study problems associated with the behavior of germanium in the course of pyrometallurgical conversion of complex sulfide ores.

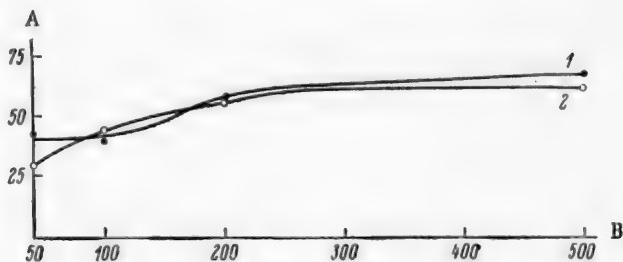


Fig. 1. Effect of amount of precipitant on the degree of precipitation. A) Amount of metal precipitated (%); B) amount of precipitant (mg); 1) precipitation of copper, 2) precipitation of germanium.

E. M. Nanobashvili, et al., drew attention to the possible formation of a double sulfide of the $\text{CuS} \cdot \text{GeS}_2$ type in a strongly acid medium. We used the radioactive Ge-71 isotope for determinations of the optimum

conditions for precipitation of copper-germanium sulfide corresponding to the formula $\text{CuS} \cdot \text{GeS}_2$. Copper was determined iodometrically. The analyses for germanium and copper were performed with the solution after precipitation of the sulfide. The experimental procedure with radioactive germanium was similar to that described earlier [6]. The activity counts were performed in a type "B" unit with the MST-17 end-type counter.

Solutions of quadrivalent germanium containing the radioactive Ge-71 isotope, and of cupric copper of the same normality, were first prepared. The solutions of copper and germanium were mixed, acidified, made up to a constant volume, and the sulfide was then precipitated by addition of solid sodium sulfide.

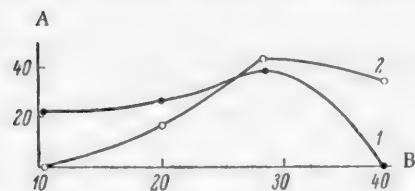


Fig. 2. Effect of solution acidity on the degree of precipitation. A) Amount of metal precipitated (%); B) solution acidity (vol. %); 1) precipitation of copper, 2) precipitation of germanium.

were closely similar, a mechanical mixture of white tetravalent germanium sulfide and black cupric sulfide was not formed. The precipitate was homogeneous, brown in color.

It is clear from Fig. 1 that even with 200 mg of precipitant the degree of precipitation is about 60% and the composition of the compound is close to $\text{CuS} \cdot \text{GeS}_2$. The degree of precipitation increases with increasing excess of precipitant. The theoretical amount of precipitant required is about 100 mg.

It follows from Fig. 2 that a sulfide of the required composition is obtained at an adequate degree of precipitation from a solution containing 25 vol. % of concentrated HCl (1:3 HCl). The same figure also shows that in a less acid medium copper sulfide is primarily precipitated, and in a more acid medium, germanium sulfide.

SUMMARY

The double sulfide of copper and germanium, close to $\text{CuS} \cdot \text{GeS}_2$ in composition, should be precipitated from a 1:3 HCl solution with 2-3 fold excess of Na_2S precipitant. Minor deviations of the copper or germanium contents from the stoichiometric proportions should have little effect on the composition of the double sulfide.

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A SIMPLE THERMOREGULATOR FOR STABILIZATION AND PROGRAM VARIATION OF TEMPERATURE

O. A. Matveev

Highly accurate temperature regulation and program variations of temperature are of great practical importance. The existing commercial thermoregulators often do not have the necessary sensitivity and accuracy.

The simple thermoregulator, the circuit of which is given in Fig. 1, is of the potentiometric type using the direct-current PP works potentiometer. Since a null instrument of high sensitivity is used as the indicator, this circuit has considerable advantages over direct-reading circuits. A germanium photodiode or a cadmium sulfide photoresistor type FSK is fixed in the potentiometer under the galvanometer needle. The distance between the photocell and the galvanometer needle is about one millimeter. A small foil flag is attached to the galvanometer needle, and one of the needle stops is moved from the end to the middle of the galvanometer scale.

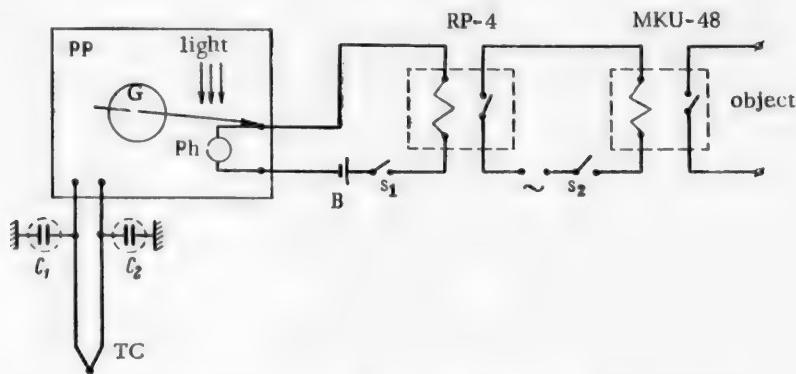


Fig. 1. Thermoregulator circuit. PP) Direct-current potentiometer; G) galvanometer; Ph) photocell; TC) thermocouple; C_1 and C_2) filter capacitors.

The germanium photodiode is fed from a Zs-L-30 battery of 1.5 v; the cadmium sulfide photoresistor requires about 100 v. The light source is a 10 v lamp to which a somewhat lower voltage is supplied. The light from the lamp is directed onto the sensitive surface of the photocell as shown in Fig. 2. The lamp filament is projected onto the flag along the galvanometer needle.

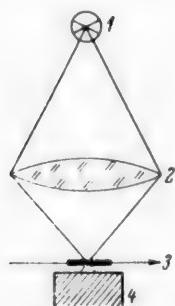


Fig. 2. Course of light rays in illuminator. 1) Light source, 2) lens, 3) galvanometer needle, 4) photocell.

The photocell is connected in series with the winding of a sensitive relay type RP-4, the contacts of which are in series with the winding of a coarse relay type MKU-48; the contacts of the latter break the object circuit.

If a large current has to be broken, a power relay is also included. The contacts of the sensitive relay are brought closer together, and the minimum current for operating the relay is thereby established. The switches S_1 and S_2 are used to disconnect the relay windings from the supply sources.

Because of the high sensitivity of this circuit, it is often necessary to connect a filter at the potentiometer input, as shown in Fig. 1. The filter consists of two electrolytic capacitors which drain to ground the various electrical signals induced in the thermocouple circuit. The thermocouple must have zero junctions and must be effectively insulated.

The required temperature is measured or preset along the potentiometer scale by rotation of the rheochord knob. If the rheochord knob is rotated at a certain rate,

constant or variable in time, then the temperature will also vary at the same rate and in accordance with the same law. For this purpose, it is sufficient to attach a gear wheel to the rheochord and to couple it with a reducing gear mechanism. This device can be used for varying rates of heating or cooling between 2°/hour and 100°/hour. The relay operates with a 50 µv change of input voltage.

Several different variants of this scheme have been constructed and used successfully in the laboratory for temperature regulation.

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THE INTENSITY OF ATMOSPHERIC CORROSION OF ROLLED FERROUS METALS AT SUBZERO TEMPERATURES

I. P. Kharlamov and G. N. Mekhovshchikova

Atmospheric corrosion of rolled ferrous metals during prolonged storage in the open occurs over a wide range of temperatures and air humidities.

The effect of relative humidity of the air on corrosion rates at positive temperatures (1-30°) has been studied fairly thoroughly [1-3]. Moisture is a constant factor in atmospheric corrosion although, according to the theory being developed by Iofa [4], it is not itself an aggressive medium.

Increase of the relative humidity above a critical value (65-70% for steel) produces a sharp acceleration of the corrosion process. The corrosion rate at high relative humidities increases with the temperature.

Atmospheric corrosion of steel at subzero temperatures has been studied much less. Some workers [5, 6] assert that corrosion is more rapid in winter than in summer. A. Dychko and K. Dychko [7], who studied the mechanism of atmospheric corrosion of metals at low temperatures, reached the opposite conclusion. Their experimental and theoretical studies showed that atmospheric corrosion is slower in winter (at low temperatures) than in summer. They found a critical temperature (-25°) below which atmospheric corrosion slows down sharply. They point out that at -25° the probability of a chemical reaction at the metal surface diminishes, as the absolute humidity of the atmosphere decreases with fall of temperature; atmospheric moisture is precipitated as rime or snow which are more neutral than water in metal corrosion; water in the corrosion products is changed into ice and its volume increases; the corrosion products thereby become denser and form an effective obstacle to bilateral diffusion of molecules from the atmosphere and surface atoms from the metal.

Our results, obtained in 1955-1956 and presented in this paper, confirm the results of A. and K. Dychko.

EXPERIMENTAL

The rate of atmospheric corrosion of low-carbon steel was studied in stands situated in one of the industrial regions of Moscow. Specimens of St 10 sheet steel, 100 × 100 × 1 mm in size, were used for the tests. The specimen surfaces were sandblasted before the tests. The specimens were fixed in the stands between four porcelain rollers at an angle of 45°. The front surfaces of the specimens faced south. The degree of corrosion was estimated from the weight loss of the specimens after removal of rust by treatment with sulfuric acid containing inhibitor.

The tests were continued for one year, from May 1955 to May 1956. The summer months of 1955 had little precipitation and high day air temperatures (up to +35°). During the winter period low air temperatures were recorded (down to -35°). There was abundant rainfall in the spring of 1956.

The weight changes of St 10 steel specimens in atmospheric corrosion tests during the annual cycle are given below.

Duration of test (days)	Period	Weight loss (g/m ²)
40	May-June 1955	63.3
70	June-July 1955	173.6
125	July-September 1955	204.6
155	September-October 1955	237.9
185	October-November 1955	307.7
305	November 1955-March 1956	371.3
392	March-May 1956	553.9

It follows from these results that the greatest weight changes are found in the period April-June, and the least, in the period December-March. The corrosion rate of the steel specimens is roughly 3 times as high in the fall and summer as in winter.

SUMMARY

Prolonged exposure tests on low-carbon steel show that atmospheric corrosion of rolled ferrous metals is considerably slower in winter at subzero temperatures.

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USE OF ORGANOSILICON COMPOUNDS FOR PAPER SIZING*

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Sizing is an essential requirement in most papers. "Sizing" in the paper industry is a process which makes the paper capable of retaining ink marks on its surface without penetration to the other side and without spreading over the surface. Cellulose fibers from which paper is made are highly hydrophilic. Aqueous solutions, including ink, are strongly absorbed by unsized paper, spread over its surface, and penetrate to the other side.

To make cellulose fibers hydrophobic, their surface is treated with water-repellent coatings. Usually such treatment is effected in the paper industry by means of rosin; the paper is treated with various rosin sizes.

Because of the high cost and scarcity of rosin, and of the various difficulties which arise in rosin sizing of paper, new sizing materials must be sought. We therefore studied organosilicon compounds for this purpose, as they can be used for conferring water repellency to various materials.

The investigation of the use of organosilicon compounds for paper sizing consisted of an examination of various treatment methods and searches for the most effective substances.

Three methods of paper treatment by organosilicon compounds were considered: a) treatment of the finished paper with methyltrichlorosilane vapor; b) impregnation of the finished paper with solutions of organosilicon compounds; c) addition of organosilicon compounds to the stock.

The treatment of paper by methyltrichlorosilane vapor was performed under laboratory conditions, with subsequent neutralization of the hydrogen chloride by means of gaseous ammonia or by addition of chemical reagents (magnesium or barium oxides, chalk, or sodium bicarbonate) to the stock. The treatment yielded paper of a high degree of sizing, with a very low reagent consumption, in a very short time (some seconds). The mechanical quality characteristics of the paper were lowered somewhat.

Disadvantages of this method are the complicated treatment procedure which requires strictly air-tight equipment, difficult operating conditions, toxicity and corrosiveness of methyltrichlorosilane, and the explosion hazard associated with mixtures of this gas and air.

Several materials were tested for impregnation of paper by organosilicon compounds. Good results were obtained with methyltriacetoxysilane (A-1), used as a solution in organic solvents at concentrations from 0.001 to 3%.

The results of these experiments showed that paper impregnated with A-1 solution shows good sizing characteristics only after heat treatment. The mechanical quality characteristics are then improved somewhat. The method requires relatively large amounts of reagent and solvent, and additional equipment for impregnation and heat treatment of the paper and for solvent recovery.

The most suitable method of using organosilicon compounds in paper manufacture is by stock sizing. Most of the work on the use of organosilicon compounds was performed in this direction. Several organosilicon compounds were investigated, some soluble in water and others insoluble and used in the form of aqueous emulsions. It was found that the best sizing effect is produced by the use of water-insoluble organosilicon compounds of the polyalkylhydrosiloxane type: EN-1, $(C_2H_5SiHO)_n$ and MN-1, $(CH_3SiHO)_n$.

The best results are obtained with MN-1. However, a high degree of sizing (2 mm) is obtained with the use of 0.5 to 3% of these compounds on the dry fiber weight only after heat treatment of the finished paper. Without heat treatment, the best degree of sizing obtained was 1-1.25 mm.

* Communication VII in the series on waterproofing of materials by organosilicon compounds.

Heat treatment under production conditions introduces complications into the process. Therefore, the purpose of the subsequent experiments was to improve the sizing of paper by treatment with organosilicon compounds without heat treatment.

The following aspects were investigated: a) variations of paper quality during storage under normal conditions, b) addition of melamine-formaldehyde resin to the paper stock or to the polyalkylhydrosiloxane emulsion, c) addition of various catalysts to the organosilicon emulsion.

Trials conducted under production conditions showed that the degree of sizing of paper treated with organosilicon compounds increases to 2 mm without heat treatment in the course of normal storage. The use of melamine-formaldehyde resin and certain catalysts (benzoyl peroxide, lead and zinc acetates, triethanolamine, zirconium salts, etc.) improves sizing quality and reduces the aging time necessary to reach a high degree of sizing. As the result of numerous experiments the minimum aging time was found to be 8-12 days. This result was obtained with the use of MN-1 organosilicon compound in presence of catalysts or of melamine-formaldehyde resin.

Further work on improvement of sizing quality and elimination of heat treatment from the technical process consisted of a search for new catalysts. Among a large number of catalysts investigated, the best results were given by sodium diethyldithiocarbamate $[(C_2H_5)_2NCSSNa]$.

Similar catalytic effects were obtained with the use of the acetates and chlorides of mercury, cadmium, cobalt, and nickel, and with potassium ethyl xanthate $[C_2H_5OCSSK]$.

These catalysts reduce the aging time of the paper, so that highly sized paper can be obtained without heat treatment.

A high degree of sizing (2 mm) can be attained immediately after manufacture of the paper, without aging or heat treatment, by partial replacement of rosin by organosilicon compounds (with a 75% decrease in the total amount of rosin). The amount of rosin is reduced for 1.8-2% on the fiber weight to 0.5%, and 1% of MN-1 organosilicon emulsion is added.

The paper so made has a stable degree of sizing (2 mm) immediately after manufacture, without heat treatment (see table).

Composition of sizing materials (% on fiber weight)	Degree of sizing (mm) without aging or heat treatment of the paper	
	by penetra-tion	by spreading
0.5 rosin + 1.5 MN-1 + 0.1 $(C_2H_5)_2NCSSNa$ + + 0.5 alumina	2.0	2.0
0.5 rosin + 1.0 MN-1 + 0.1 $(C_2H_5)_2NCSSNa$ + + 0.5 alumina	2.0	2.0
0.5 rosin + 0.5 alumina	0.0	0.25

The experiments showed that it is better to add the catalyst to the paper stock rather than to the emulsion.

As the result of this work, the problem of paper sizing by means of organosilicon compounds may be regarded as solved. Stock sizing of paper is a practical method which should be adopted. The polymerization may be accelerated by brief heat treatment or by the use of catalysts.

It should be noted that filler retention is considerably increased by stock sizing with polyalkylhydrosiloxanes; this is very important in the production of printing papers.

The authors are deeply grateful to Professor B. N. Dolgov for his interest in this investigation.

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COMPARATIVE STUDY OF THE EFFECTS OF TRISODIUM PHOSPHATE,
SODIUM PYROPHOSPHATE, AND SODIUM HEXAMETAPHOSPHATE ON
THE STABILITY OF RESIN - WATER AND RESIN - SULFITE LIQUOR -
WATER SYSTEMS*

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Derevyagina and Talmud [4] studied the effect of trisodium phosphate on the systems resin - water and resin - sulfite liquor - water, and found that the stability of the system resin - sulfite liquor - water is lowered sharply by addition of trisodium phosphate. It was suggested that trisodium phosphate may be an agent which could reduce resin difficulties in paper manufacture by lowering the aggregative stability of the resin in the cellulose pulp and thus favoring coagulation of the resin in the production cycle.

Talmud and Turzhetskaya [2] suggested that the consumption of $\text{Al}_2(\text{SO}_4)_3$ or $\text{KA}_1(\text{SO}_4)_2$ can be diminished by addition of small amounts of trisodium phosphate before coagulation, on the hypothesis that the stability of emulsified resin in paper stocks and liquors is closely associated with the presence of surface-active substances from sulfite liquor in the pulp. Experiments confirmed this hypothesis, and showed that the coagulant consumption can be reduced by 35-50%. It was concluded that the coagulation method proposed earlier, with the use of $\text{KA}_1(\text{SO}_4)_2$ and $\text{Ca}(\text{OH})_2$, and preliminary addition of Na_2PO_4 , provides the optimum conditions for coagulation of emulsified resin and maximum retention of kaolin in the paper.

Booth [5] found that it is desirable to add dispersing agents, such as pyro- and metaphosphates and other substances which improve the colloidal properties of clays, to starch-clay mixtures.

Kerr [6] reports that when very small amounts of such alkaline wetting agents as tetrasodium pyrophosphate are added to an almost solid mass consisting of two parts of kaolin and one part of water, the mixture is converted into a free-flowing suspension.

Gavelin [7] found that sodium hexametaphosphate $[\text{NaPO}_3]_6$ is an interesting means of preventing resin difficulties. He considers that at a definite concentration of hexametaphosphate a phosphate film preventing resin deposition is formed on surfaces in contact with the production liquors. Moreover, the phosphate also acts on the emulsified resin and assists retention of its particles in the layer of stock during dewatering.

The purpose of the present work was to study the effects of trisodium phosphate, sodium pyrophosphate, and sodium hexametaphosphate on the stability of emulsified resin in resin - water and resin - sulfite liquor - water systems, and to compare the relative effectiveness of these substances.

EXPERIMENTAL

The effect of phosphates on the stability of the systems was studied by the method described previously [4]. The least amounts of aluminum sulfate required for complete coagulation of the emulsified substances were determined. These values were a measure of the stabilizing power of the phosphates.

The results of the experiments are summarized in the table.

It should be noted that if the amount of added sodium hexametaphosphate is increased, instead of complete transparency of the system, corresponding to complete coagulation, an intense turbidity appears, and does not disappear even at very high concentrations of added aluminum sulfate.

Several important conclusions may be drawn from the tabulated data. Coagulation of emulsified resin in the resin - water system occurs on addition of very small amounts of aluminum sulfate. Introduction of any of the

* Communication XIII in the series on resin difficulties in the pulp and paper industry. For Communications X, XI, and XII, see [1-3].

Effects of Na_3PO_4 , $\text{Na}_4\text{P}_2\text{O}_7$, and $[\text{NaPO}_4]_0$ on Stability of Resin - Water and Resin - Sulfite Liquor - Water Systems

System	Resin content of emulsion wt. %	Amount of $\text{Al}_2(\text{SO}_4)_3$ required for complete coagulation mmole/liter	Contents of				Notes
			$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ • mmole/liter	wt. %	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ • mmole/liter	wt. %	
Resin - water	0.0385	0.125	0.004	0.261	0.004 (0.01)	—	—
		0.125	0.004	—	0.218	0.006 (0.01)	0.01
Resin - sulfite liquor (0.05 wt. %) - water	0.048	20.0	0.845	0.261	0.004 (0.01)	—	No complete coagulation
		0.425	0.004	—	0.198	0.006 (0.01)	—
Resin - sulfite liquor (0.1 wt. %) - water	0.056	11.00	0.422	—	—	—	—
		11.00	0.422	—	—	—	—
Resin - sulfite liquor (0.25 wt. %) - water	0.073	20.0	0.845	0.173	0.004 (0.01)	—	—
		1.200	0.042	—	—	—	—
Resin - sulfite liquor (0.5 wt. %) - water	0.117	11.00	0.422	—	—	—	—
		11.00	0.422	—	—	—	—

• Calculated as anhydrous salt; values as the hydrate in parentheses.

phosphates under investigation has no effect on the stability of this system. The stability is increased sharply, as is to be expected, on addition of various amounts of sulfite liquor.

Addition of each of the phosphates to the system water—sulfite liquor—water decreases stability, but to different extents.

It follows that trisodium phosphate, sodium pyrophosphate, and sodium hexametaphosphate are destabilizers or sensitizers for the system resin—sulfite liquor—water.

The effect of sodium pyrophosphate is very similar to the effect of trisodium phosphate, but the amount of sodium pyrophosphate required for destabilization becomes considerably more than the amount of trisodium phosphate with increased stability of the system.

The least effective destabilizer is sodium hexametaphosphate, and the consumption of sodium hexametaphosphate therefore rises sharply with increase in the stability of the system. It is possible that sodium hexametaphosphate has other effects apart from its destabilizing action. However, this question was not examined. Thus, of the phosphates investigated the best destabilizer is trisodium phosphate, and its consumption for destabilization of the systems is the lowest.

These results may be regarded as additional evidence in favor of the choice of trisodium phosphate for destabilization of emulsified and suspended substances in stocks and liquors of the paper industry.

SUMMARY

1. The effects of trisodium phosphate, sodium pyrophosphate, and sodium hexametaphosphate on the stability of emulsified resin in resin—water and resin—sulfite liquor—water systems were studied; it is shown that all three phosphates are destabilizers or sensitizers for the system resin—sulfite liquor—water.

2. The effectiveness of these phosphates as destabilizers can be represented by the following decreasing series: $\text{Na}_3\text{PO}_4 > \text{Na}_4\text{P}_2\text{O}_7 > [\text{NaPO}_3]_6$.

Smaller amounts of trisodium phosphate than of the other phosphates are required for destabilization.

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SYNTHESIS OF N-SULFONYL-p-TOLYL-N'-BUTYLUREA

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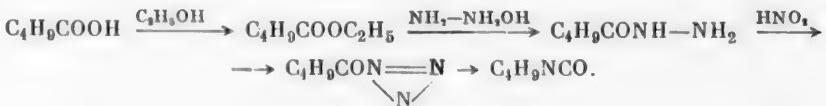
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Recently many publications have appeared in the Russian and foreign literature [1] on the use of sulfonamide derivatives of alkyl ureas for treatment of diabetes mellitus (N-sulfanilyl-N'-butylurea, N-sulfonyl-p-tolyl-N'-butylurea). Of these, N-sulfonyl-p-tolyl-N'-butylurea proved to be the most effective. This substance can in many cases be used instead of the natural hormone, insulin; its action on the patient produces no toxic side effects, and it can be administered by the mouth. This substance is marketed abroad by many firms under various trade names (tolbutamide, D 860, rastinon, orinase, U 2043, etc.). The method of its preparation has not been published; there is only one patent on the production of a sulfonamide derivative of methylurea.

Our aim was to develop a convenient laboratory and semi-production method for synthesis of N-sulfonyl-p-tolyl-N'-butylurea. Sulfonamide derivatives of urea are prepared by the following reaction of sulfonamides with alkyl isocyanates [3]:



We therefore devoted our attention to the development of a convenient laboratory method for preparation of butyl isocyanate. From the methods described in [4] we chose the Curtius reaction [5]



EXPERIMENTAL

The method described for preparation of DL-methylethylacetic acid [6] was used for synthesis of n-valeric acid. It was synthesized from commercial butyl bromide, which was first dried over calcium chloride and distilled. B. p. 100-101°. The yield of n-valeric acid was 70-73% of the theoretical yield calculated on the butyl bromide taken.

Ethyl valerate was prepared by a known method [7]. B. p. 145°, yield 82-86% of the theoretical, calculated on valeric acid.

Valeryl hydrazide. 110 g (0.85 mole) of ethyl valerate was added gradually to 51.8 g (1.04 mole) of hydrazine hydrate in a round-bottomed flask fitted with a reflux condenser. The rate of addition was regulated so that each successive portion of the ester was added only after the previous portion had mixed completely with the hydrazine hydrate. The reaction mixture was then heated for 16 hours and poured out into a basin, where it crystallized on cooling. M. p. 60°, yield of valeryl hydrazide 97.4 g (99.3% of the theoretical on valeryl hydrazide).

Valeryl azide. To 83.7 g of valeryl hydrazide, dissolved in 1496 ml of 1 N hydrochloric acid, 50.2 g of sodium nitrite dissolved in 317 ml of water was added at a rate such that the temperature of the reaction mass did not exceed 10°. The mass was then stirred for 30 minutes; the valeryl azide was extracted in benzene and dried thoroughly by means of calcium chloride.

Butyl isocyanate was prepared by the action of heat on a solution of valeryl azide in benzene for 2 hours on a boiling water bath. Butyl isocyanate was used in the next step in the form of a solution in benzene.

N-sulfonyl-p-tolyl-N'-butylurea. The p-toluenesulfonamide required for the synthesis was prepared from commercial p-toluenesulfonchloride by treatment with aqueous ammonia. M. p. 137°.

A mixture of 100 g of p-toluenesulfonamide, 175 g of anhydrous potash, and 1000 ml of dry acetone was put in a flask fitted with a stirrer and condenser. The mixture was stirred for 1 hour 30 minutes at 50°. The previously prepared benzene solution of butyl isocyanate was then added slowly (with thorough stirring at 50°). The mixture was stirred for an additional 4 hours 30 minutes, filtered, and the acetone was distilled off. The residue after distillation of the acetone was treated with water and filtered to remove unreacted p-toluenesulfonamide. The filtrate was acidified with hydrochloric acid and the separated N-sulfonyl-p-tolyl-N'-butylurea was filtered off. After recrystallization from aqueous alcohol the substance melted at 126-128°. Yield 117 g (60% of the theoretical calculated on valeryl hydrazide).

Found %: SO₂NH 29.33, 29.13; N 10.5, 10.4. Calculated %: SO₂NH 29.2; N 10.37 [8].

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A CONVENIENT METHOD FOR SYNTHESIS OF TRIFLUOROACETIC ACID

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Several methods for preparation of trifluoroacetic acid are described in the literature. For example, Swartz [1] recommends oxidation of m-aminobenzotrifluoride by chromic acid. Henne [2, 3] oxidized 1,1,1-trifluorochloropropene by alkaline potassium permanganate solution. Babcock and Kischitz [4] described the analogous oxidation of fluorochlorobutenes, such as 1,1,1,4,4,4-hexafluoro-2,3-dichlorobutene-2. Recently methods have been described for preparation of trifluoroacetic acid by electrolysis of acetic anhydride in hydrogen fluoride [5] and by hydrolysis of 2,4,6-tri(trifluoromethyl)-1,3,5-triazine by dilute mineral acid [6].

It follows from the foregoing that some of the above methods for synthesis of trifluoroacetic acid involve the preparation of fluorides which are not easily available (trifluoropropene or trifluorobutene derivatives, tri(trifluoromethyl)triazine) and others require special apparatus (electrochemical fluorination).

We have developed a convenient method for synthesis of trifluoroacetic acid from 1,1,1,3-tetrachloropropane. The latter, as is known, is easily obtained together with other tetrachlorides by the telomerization reaction of ethylene with carbon tetrachloride [7]. Tetrachloropropene is converted easily and in good yields

into trifluorochloropropane [8] and subsequently into trifluoropropene [9]. We found that when trifluoropropene is oxidized by alkaline potassium permanganate solution trifluoroacetic acid is obtained in 80% yield. This synthesis is described below.

Preparation of antimony trifluorodichloride [10]. 400 g of antimony trifluoride was put in a 0.5 liter autoclave and gaseous chlorine (from a cylinder) was passed in at 135° with stirring. A steady pressure (approximately 5 atmos) in the autoclave indicated the end of the reaction. The yield was 96-97%.

Fluorination of tetrachloropropane. 165 g of powdered antimony trifluoride and 190 g of antimony trifluorodichloride was put in a three-necked flask. 250 ml of dry dichloroethane was added with stirring, the flask being cooled in water and, with continued cooling, 250 g of pure tetrachloropropane was then added dropwise; the stirring was continued for 1-2 hours more and the product was distilled in steam. The lower distillate layer was separated off, dried, and distilled twice. The yield of trifluorochloropropane of b. p. 46° and $n^{20}D = 1.336$ was 58-63% (according to Haszeldine, b. p. 45-46°, $n^{20}D = 1.334$).

Preparation of trifluoropropene. To a saturated solution of 47 g KOH in ethyl alcohol 100 g of trifluorochloropropane was added gradually with stirring at 0°. The yield of trifluoropropene of b. p. -22° was 98% of the theoretical.

Preparation of trifluoroacetic acid. Into a solution of 260 g $KMnO_4$ and 3 g KOH in 4 liters of water at 80° about 15 liters of trifluoropropene was passed from a gas holder with vigorous stirring at a rate of 2-3 liters per hour. Toward the end of the reaction the trifluoropropene rate was decreased so that break-through of trifluoropropene was reduced to a minimum. The reaction solution was then cooled to room temperature, SO_2 was passed through it until it became colorless, and saturated sodium carbonate solution was added until the liquid was alkaline to litmus. The precipitate was filtered off and washed with hot water, and the filtrate was evaporated to dryness. The trifluoroacetate was extracted from the dry residue by boiling absolute alcohol (200 ml). The alcohol was distilled off (the last stages under vacuum). Concentrated H_2SO_4 was added dropwise to the salt (bath temperature 130°) and pure trifluoroacetic acid was distilled off; its b. p. was 72.4°, $n^{20}D = 1.486$. The yield was approximately 80% of the theoretical calculated on trifluoropropene.

SUMMARY

It is shown that trifluoroacetic acid is obtained in 80% yield by oxidation of trifluoropropene by alkaline potassium permanganate solution.

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SPECIAL INDICATOR TUBES FOR RAPID DETERMINATION OF NITROGEN OXIDES IN THE AIR OF INDUSTRIAL BUILDINGS

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Detection and quantitative determination of nitrogen oxides in industrial buildings, during production of nitrile and sulfuric acids, nitration and nitrosation of organic compounds, production of azo dyes, and other operations is of great importance from the hygienic and technical aspects. In view of the fact that determinations of nitrogen oxides are carried out fairly frequently for these purposes, it is necessary to have simple and rapid determination methods which do not require special knowledge or preparation.

The literature contains a considerable number of methods for determination of nitrogen oxides, based on the use of the Griess-Ilosvay reagent, etc. [1-3]. In these methods nitrogen oxides are determined in the liquid phase; there are also methods involving the use of carriers on which various chemical substances are adsorbed; these change color in presence of nitrogen oxides. Filter paper impregnated with alcoholic benzidine solution has been recommended as the carrier [4]. Others have recommended silica gel as carrier, with adsorbed Griess-Ilosvay reagent [5]. If air containing nitrogen oxides is passed through, the color of the indicator changes. The content of nitrogen oxides is estimated either from the change in the color intensity, or by measurement of the thickness of the colored indicator layer [6].

Investigations carried out by Filippychev and Petrov [7] on the action of nitrogen oxides on amino compounds showed that aromatic amines are readily diazotized in the dry state in presence of nitrogen oxides. This result was used for the development of a method, proposed by us earlier [8], for determination of nitrogen oxides and p-aminobenzoic acid. The principle of the determination of nitrogen oxides is that when air containing nitrogen oxides is passed through a solution of p-aminobenzoic acid the latter is diazotized. Subsequent coupling of the diazotized p-aminobenzoic acid with H acid yields a stable crimson dye, the color intensity of which depends on the concentration of nitrogen oxides in the air.

This reaction has certain advantages over the widely-used Griess-Ilosvay method, but it is conducted in the liquid phase, which is an obstacle to its extensive utilization; therefore, we used this principle and certain literature data [7] to develop a rapid method for determination of nitrogen oxides by means of indicator tubes [9]. For this test, H acid, p-aminobenzoic acid, and nickel chloride were adsorbed on silica gel. In presence of nitrogen oxides this indicator gel changes its color from pale pink to crimson-brown; the shade differs in accordance with the concentration of nitrogen oxides. In this reaction a diazonium salt is formed by the action of nitrogen oxides on p-aminobenzoic acid. When this salt is coupled with H acid, which is the azoic coupling component while nickel chloride is the catalyst, a dye is formed.

For preparation of the indicator gel 1 g of silica gel is taken, 20 ml of saturated alcoholic solution of H acid is added, and the mixture is stirred for 2 minutes while the alcohol evaporates off; 20 ml of 0.5% alcoholic solution of p-aminobenzoic acid is added to the mass; the mass is dried and stirred, 0.5 ml of 0.1% alcoholic solution of nickel chloride is added, and the indicator mass is dried to a powder with stirring.

The indicator gel is used for preparation of the indicator tubes; for this, a glass tube 80-100 mm long and 3-5 mm inner diameter is taken, and one end is drawn out to a point and sealed. A cotton-wool or glass-wool plug is introduced at the wide end, pushed through to the pointed end, tamped down slightly, and covered with a 3 mm layer of calcined quartz sand or silica gel. A 2 mm layer of indicator gel is then put in the tube; this is covered with a 2 mm layer of sand or silica gel and tamped down; a cotton-wool or glass-wool plug is put in, packed down slightly by means of a glass rod, and the wide end of the tube is sealed. Such indicator tubes can be stored for a long time.

For determination of nitrogen oxides in air a tube is opened at both ends, and 100 ml of the air is blown through from the wide end in the direction of the pointed end. When this amount of air has been passed, the color of the indicator is compared with a standard colorimetric scale, and the amount of nitrogen oxides in mg/liter is found.

For preparation of the color standards, 100 ml lots of air containing known concentrations of nitrogen oxides are passed through the indicator tubes; the tubes are sealed and kept as standards or the standard colors are reproduced on paper.

Results of Nitrogen Oxide Determinations by Means of Indicator
Tubes and By The Griess-Ilosvay Method

Calculated concentration for volume used (mg/liter) *	Concentration determined colorimetrically by the Griess-Ilosvay method (mg/liter)	Concentration determined by indicator tubes (mg/liter)
0.00056	0.00055	0.0005
0.0028	0.0028	0.003
0.0034	0.0033	0.003
0.0053	0.0051	0.005
0.0055	0.0053	0.005
0.087	0.1	0.085
0.09	0.093	0.9
0.095	0.097	0.1
0.1	0.098	0.1
0.1	0.12	0.1

* Nitrogen oxides were prepared in the reaction space by the action of sodium nitrite on hydrochloric acid.

The sensitivity of these indicator tubes was determined by the Griess-Ilosvay standard method; it was found to be 0.0005 mg/liter.

The standard colors were used to compare the results obtained by the Griess-Ilosvay method and by means of the indicator tubes. The results are given in the table.

It is seen that satisfactory results were obtained in the comparison of these methods, so that the indicator tubes may be recommended for determination of nitrogen oxides.

To test the specificity of the reaction, we passed vapors of ether, hydrochloric acid, mercury, and carbon disulfide, and also nitrogen, ammonia, and carbon monoxide gases, through the indicator tubes. The color of the indicator tubes was not changed by contact with these substances.

The temperature of industrial buildings (between 10 and 25°) and variations of relative humidity in the 40-90% range did not influence the results.

Thus, the indicator tubes, which are simpler to use, may be used for determination of nitrogen oxides in the air of industrial buildings, in addition to existing methods.

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HYDROGEN OVERVOLTAGE ON MULTIPHASE ELECTRODES

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The electrodes used in technical electrolysis and in chemical sources of current are in the great majority of cases multicomponent systems, consisting of the principal metal and impurities or specially introduced additives.

It would be very useful to be able to determine quantitatively the influence of these impurities or additives on the hydrogen overvoltage, which is an important electrochemical electrode characteristic; in many cases such determination would serve as a criterion of the applicability of a particular electrode for effective operation of a particular electrochemical process on it.

However, with rare exceptions, such possibilities do not exist, owing to formation of chemical compounds and solid solutions in the electrode material; these introduce complications, which cannot as yet be considered quantitatively, into the problem.

Because of this, hydrogen overvoltage on technical electrodes can be determined experimentally only at present. Important determinations in this field have been performed by Stender and Pecherskaya [1].

The exceptions are electrodes which consist of multiphase systems, such as sintered metal compositions, which are now finding practical uses in applied electrochemistry.

The surface of a multiphase electrode may be regarded as consisting of a large number of regions of different components, with electrochemical properties (hydrogen overvoltage) characteristic of the given pure components. If the electrode is considered in this manner and the equipotentiality of the electrode surface is taken into consideration, a quantitative expression can be derived for calculation of hydrogen overvoltage on a multiphase electrode from known experimental values for hydrogen overvoltage on the pure metals which constitute the electrode. If the relevant experimental data are not available, the hydrogen overvoltages can be calculated theoretically from the Lorentz formula [2] with the use of the compressibility coefficients of the pure metals.

For two-phase electrodes, this type of calculation based on experimental values of hydrogen overvoltage on the pure metals gives the expression [3]

$$\Delta\varphi = \varphi_{2p} - \varphi_1 = b \ln \frac{(A+1)n}{n+1}, \quad (1)$$

where $\Delta\varphi$ is the difference between the potentials of hydrogen evolution on the two-phase system (φ_{2p}) and on the pure metal (φ_1); A is a constant which depends on b , a_1 , a_2 , and n .

$$A = \frac{\exp\left(\frac{a_1 - a_2}{b}\right)}{n},$$

where b , a_1 , and a_2 are respectively the prelogarithmic coefficient and the constants of the Tafel equation for metals 1 and 2; n is the ratio of the areas of the electrode surface S_1 and S_2 occupied by metals 1 and 2, respectively ($n = \frac{S_1}{S_2}$; $S_1 + S_2 = 1$).

This equation has been confirmed experimentally [3, 4].

For further derivations, Eq. (1) is conveniently written as:

$$\Delta\varphi = \varphi_{2p} - \varphi_1 = b \ln [(A_{1p_2} - 1) S_2 + 1], \quad (2)$$

where $A_{1p_2} = nA$, as before, refers to a two-phase system consisting of metals 1 and 2.

It is known that the potential of hydrogen evolution at an electrode can be represented by the difference between the equilibrium potential (φ_e), which is a function of the solution composition and is independent of the electrode material, and the hydrogen overvoltage (η) at the same electrode. Applying this rule to φ_{2p} and φ_1 in Eq. (2), we can write

$$\Delta\varphi = (\varphi_e - \eta_{2p}) - (\varphi_e - \eta_1), \quad (3)$$

and hence, with Eq. (2) taken into account, it follows that

$$\eta_{2p} = \eta_1 - \Delta\varphi = a_1 + b \ln i_1 - b \ln [(A_{1p_2} - 1) S_2 + 1]. \quad (4)$$

If we write

$$a_{2p} = a_1 - b \ln [(A_{1p_2} - 1) S_2 + 1], \quad (5)$$

then Eq. (4) for hydrogen overvoltage at a two-phase electrode assumes the usual form of the Tafel equation for overvoltage in phase 1, the constant a in which incorporates dependence on the hydrogen overvoltage on the two phases (A_{1p_2}) and on the fraction of the electrode surface occupied by phase 2 (S_2), i.e., on the composition of the electrode surface.

The foregoing considerations lead to the conclusion that a two-phase system can be reduced to a one-phase system in terms of the Tafel equation. This fact, in turn, makes it possible to generalize Eq. (5) for hydrogen overvoltage at an electrode consisting of a system of any number of phases. Thus, a three-phase system can be reduced to a two-phase one if phases 1 and 2 are considered as a one-phase system to which phase 3 has been added.

The equation for a three-phase system, analogous to Eq. (5), assumes the form:

$$a_{3p} = a_{2p} - b \ln [(A_{2p_3} - 1) S_3 + 1], \quad (6)$$

where the subscript of the constant A indicates that it refers to a system consisting of three phases two of which have been nominally considered as one.

Substituting into Eq. (6) the value of a_{2p} from Eq. (5) and using the properties of logarithmic sums, we have

$$a_{3p} = a_1 - b \ln [(A_{1p_2} - 1) S_2 + 1] [(A_{2p_3} - 1) S_3 + 1], \quad (7)$$

where •

$$A_{2p^3} = \frac{A_{13}}{(A_{1p^2} - 1) S_2 + 1} ; \quad (8)$$

here S_3 is the fraction of the electrode surface occupied by Phase 3.

Analogously, it is possible to derive an expression for the coefficient a for a four-phase system, which is considered as a two-phase one, phases 1, 2, and 3 being combined in one phase to which phase 4 is added.

The equation, analogous to Eq. (7), for a four-phase system is:

$$a_{4p} = a_1 - b \ln [(A_{1p^2} - 1) S_2 + 1] [(A_{2p^3} - 1) S_3 + 1] [(A_{3p^4} - 1) S_4 + 1], \quad (9)$$

where the subscript of the constant A in the last term indicates that it refers to a system consisting of four phases the first three of which have been nominally considered as one.

Here ••

$$A_{3p^4} = \frac{A_{1,4}}{[(A_{1p^2} - 1) S_2 + 1] [(A_{2p^3} - 1) S_3 + 1]} . \quad (10)$$

The value of A_{3p^3} is calculated from Formula (8), S_4 is the fraction of the electrode surface occupied by phase 4.

Finally, generalization of these formulas for a system with any number of phases, m , gives

$$a_{mp} = a_1 - b \ln \prod_{i=2}^m [(A_{(i-1)p} - 1) S_i + 1]. \quad (11)$$

Equations (5), (6), and (9) may be derived as special cases from Eq. (11). The coefficient $A_{(i-1)p,i}$ may be calculated from a recurrence formula, which is the general form of Eqs. (8) and (10)

$$A_{(m-1)p,m} = \frac{A_{1m}}{\prod_{i=2}^{m-1} [(A_{(i-1)p,i} - 1) S_i + 1]} . \quad (12)$$

In Eqs. (11) and (12) S_i represents the fraction of the electrode surface occupied by the i -th phase. Evidently,

$$A_{2p^3} = \exp \left(\frac{a_2 p - a_3}{b} \right) = \frac{\exp \left(\frac{a_1 - a_3}{b} \right)}{\exp \ln [(A_{1p^2} - 1) S_2 + 1]} = \frac{A_{1,3}}{(A_{1p^2} - 1) S_2 + 1} ;$$

$$A_{13} = \exp \left(\frac{a_1 - a_3}{b} \right) .$$

$$\begin{aligned} A_{3p^4} &= \exp \left(\frac{a_3 p - a_4}{b} \right) = \frac{\exp \left(\frac{a_1 - a_4}{b} \right)}{\exp \ln [(A_{1p^2} - 1) S_2 + 1] [(A_{2p^3} - 1) S_3 + 1]} = \\ &= \frac{A_{1,4}}{[(A_{1p^2} - 1) S_2 + 1] [(A_{2p^3} - 1) S_3 + 1]} ; \quad A_{1,4} = \exp \left(\frac{a_1 - a_4}{b} \right) . \end{aligned}$$

$$\sum_{i=1}^m s_i = 1, \text{ and } A_{1m} = \exp\left(\frac{a_1 - a_m}{b}\right).$$

The derived equations are evidently valid if the prelogarithmic coefficients in the Tafel equation are the same for all the phases of a given system; however, this condition is satisfied fairly accurately in most instances [5].

Another important condition for applicability of these equations is the assumption of the simplest mechanism of hydrogen liberation at a multiphase electrode, such that all the discharge steps occur consecutively on every section of the electrode, corresponding to any i -th phase.

It should be noted that the derived equations are in general applicable not only to calculations of hydrogen overvoltage but also to other electrode processes, such as oxygen overvoltage, on multiphase electrodes, if the kinetics of such processes can be represented by an equation analogous to the Tafel equation in form. The equations were verified for a number of lead-silver and lead-antimony-silver alloys.

SUMMARY

The equation derived for calculation of hydrogen overvoltage on two-phase electrodes [3] was used to show that hydrogen overvoltage can be theoretically calculated for electrodes comprising systems of any number of phases.

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INVESTIGATION OF SPECIFIC CONDUCTANCE OF AQUEOUS $\text{NaCl}_{\text{sat}} + \text{NaOH}$ SOLUTIONS IN THE 75-95° RANGE

V. A. Kuznetsov, A. A. Antipina, and R. I. Buryakovskaya

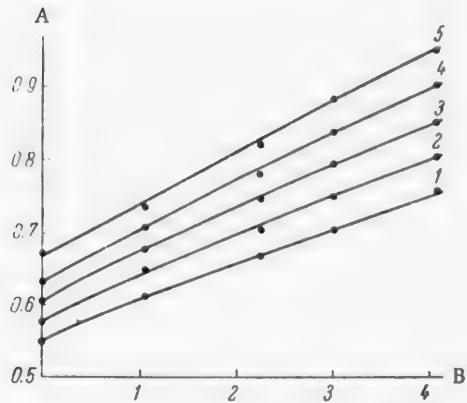
The A. M. Gor'kii State Institute of the Urals

The literature contains no data on the specific conductance of aqueous solutions saturated with NaCl and containing NaOH, in the 75-95° range. Nevertheless, such data are of undoubted interest for design calculations of cells used for electrolysis of aqueous solutions of common salt. We therefore studied the specific conductance of the system $\text{NaCl}_{\text{sat}} + \text{NaOH}$ in the 75-95° range. The results of this study are given below.

EXPERIMENTAL

The starting material was sodium chloride (chemically pure grade) recrystallized twice from redistilled water. Saturated NaCl solutions were prepared as follows. Redistilled water was put in a flask and NaCl was added until an undissolved residue appeared. The solution was stirred at intervals during 4-5 days at room temperature.

The flask was then placed in a thermostat and kept at the experimental temperature for 8-10 hours with continuous stirring of the solution. At the end of the stirring the solution was left to settle for 1 hour, when a small portion was used for conductance measurements and the rest was electrolyzed with a mercury cathode. The mercury used for the cathode was previously purified by a chemical method and distilled under vacuum. The sodium amalgam formed was thoroughly washed with redistilled water and then decomposed by saturated NaCl solution under conditions such that contact between solution and air was excluded. To accelerate the decomposition, the vessel with the solution and amalgam was warmed on a water bath, and the amalgam was short-circuited with a platinum electrode immersed in the NaCl solution. Portions of the solution were taken at intervals by means of a siphon for determination of NaOH content. When the required NaOH concentration had been reached, a certain amount of the solution was transferred to the cell for conductance determinations. The side tubes of the cell always contained a small amount of undissolved NaCl crystals. To prevent possible absorption of CO_2 , the vessel was closed by means of ground-glass stoppers. The



Specific conductance of $\text{NaCl}_{\text{sat}} + \text{NaOH}$ solutions at different temperatures. A) Specific conductance ($\text{ohm}^{-1} \cdot \text{cm}^{-1}$); B) NaOH concentration in saturated NaOH solution (M). Temperature (in °C): 1) 75, 2) 80, 3) 85, 4) 90, 5) 95.

conductance cell was of the design used by Jones and Bollinger [1]. The cell capillary was 0.7 mm in diameter and 70 mm long. With this size of capillary the resistance of the solution between the electrodes always exceeded 1000 ohms, and therefore, electrode polarization could not have any appreciable influence on the results. The platinum electrodes were covered with a thick layer of platinum black and then subjected to prolonged cathodic polarization in H_2SO_4 solution. The H_2SO_4 solution was then decanted off, and the cell was washed out thoroughly with redistilled water and steamed for 24 hours. For the measurements the cell was immersed in a thermostat with temperature fluctuations not exceeding $\pm 0.05^\circ$. The solution resistance was measured by means of the Kohlrausch bridge. The alternating-current source was an audio-frequency tube oscillator. The detector was a low-resistance telephone, the sensitivity of which was increased by means of a dual audio-frequency resistance amplifier.*

* The amplifier was assembled by G. Arkhipov, to whom we offer our thanks.

Specific Conductance of $\text{NaCl}_{\text{sat}} + \text{NaOH}$ Solutions

Temp. (in $^{\circ}\text{C}$)	Specific conductance ($\text{ohm}^{-1} \cdot \text{cm}^{-1}$) of saturated NaCl solutions with added NaOH (moles/liter):				
	0	1.054	2.244	3.01	4.08
75	0.5482	0.6121	0.6655	0.7049	0.7557
80	0.5771	0.6508	0.7014	0.7435	0.8020
85	0.6073	0.6761	0.7441	0.7932	0.8537
90	0.6342	0.7052	0.7759	0.8362	0.9035
95	0.6671	0.7324	0.8204	0.8836	0.9490

RESULTS

The specific conductance of solutions saturated with NaCl and containing NaOH (from 0 to 160 g/liter) was determined at 75, 80, 85, 90, and 95°. The results are given in the table and the diagram.

Mathematical analysis of the results gave the following expressions for the specific conductance of solutions in the investigated range of NaOH concentrations:

$$\begin{aligned} \text{at } t = 75^{\circ} \quad x &= 0.5482 + 0.06826 \cdot C - 0.00829 \cdot C^2 + 0.000988 \cdot C^3, \\ \text{at } t = 80^{\circ} \quad x &= 0.5771 + 0.08207 \cdot C - 0.01326 \cdot C^2 + 0.001631 \cdot C^3, \\ \text{at } t = 85^{\circ} \quad x &= 0.6073 + 0.0703 \cdot C - 0.00765 \cdot C^2 + 0.001174 \cdot C^3, \\ \text{at } t = 90^{\circ} \quad x &= 0.6342 + 0.0664 \cdot C + 0.00108 \cdot C^2 - 0.000295 \cdot C^3, \\ \text{at } t = 95^{\circ} \quad x &= 0.6671 + 0.0525 \cdot C + 0.0107 \cdot C^2 - 0.001625 \cdot C^3, \end{aligned}$$

where C is the NaOH concentration (moles/liter) at 20°.

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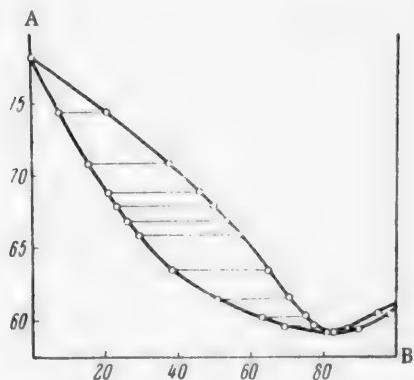
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LIQUID - VAPOR EQUILIBRIUM IN THE SYSTEM CHLOROFORM -
ETHYL ALCOHOL

A. G. Morachevskii and R. Sh. Rabinovich

The published data on solution - vapor equilibrium for the system chloroform - ethyl alcohol refer only to isothermal conditions, at 35, 45, and 55° [1].

The present communication contains the results of equilibrium studies in this system under isobaric conditions, at 760 mm Hg.



Variation of boiling point of the solution with chloroform content. A) Boiling point (in °C); B) chloroform content (molar %).

CHCl ₃ content (molar %)		Boiling point (° C) at 760 mm
in solution	in vapor	
0.0	0.0	78.30
7.5	20.3	74.60
15.6	37.5	70.95
20.4	45.9	68.85
23.0	49.9	67.90
26.5	53.3	66.90
29.5	56.9	65.90
38.2	64.5	63.60
50.6	70.7	61.50
63.3	75.2	60.15
69.3	77.0	59.75
80.7	82.3	59.25
83.1	83.4	59.20
89.5	87.2	59.55
98.0	95.0	60.50
100.0	100.0	61.20

The substances were purified before use. Chloroform was treated with concentrated sulfuric acid, washed, dried over calcium chloride, and distilled through a fractionating column of about 20 theoretical plates efficiency. The purified product had refractive index $n^{20}D$ 1.4460 and density d_4^{20} 1.4891. Rectified ethyl alcohol was treated with metallic calcium, and traces of water were then removed by azeotropic rectification with benzene. The product had $n^{20}D$ 1.3614 and d_4^{20} 0.7894.

The condensate composition was determined refractometrically. The refractive index was measured to an accuracy of 0.0001 unit in the value of $n^{20}D$. The refractive indices of solutions made up by weight in order to obtain data for the $n^{20}D$ composition curve are given below.

CHCl ₃ content (molar %)	0.00	7.86	19.35	29.80	31.05	39.09	48.50	61.24	76.07	86.30	100.00
$n^{20}D$	1.3614	1.3710	1.3837	1.3935	1.3945	1.4017	1.4094	1.4191	1.4306	1.4376	1.4460

Liquid - vapor equilibrium data were determined with the aid of Bushmakin's single-evaporation apparatus [2], which permits simultaneous determinations of boiling point and equilibrium-vapor composition. A constant pressure of 760 mm Hg was maintained by means of a manostat. The experimental results are given in the table and plotted in the figure.

According to our results the azeotropic mixture contains 83.5 molar % chloroform, whereas Horsley's book gives a value of 83.1 molar %.

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THE PROTECTIVE ACTION OF A VOLATILE CORROSION INHIBITOR — DICYCLOHEXYLAMMONIUM NITRITE

S. A. Gintsberg

Dicyclohexylammonium nitrite (DICHAN) is used as an inhibitor of atmospheric corrosion of ferrous metals during storage in vapor-impermeable packing [1]. According to [2] iron completely immersed in an aqueous solution of the inhibitor does not corrode when the inhibitor concentration is 0.1%, and corrosion is only barely perceptible at 0.01% concentration. The mechanism of the protective action of DICHAN in air, according to the manufacturer [3], depends on the fact that the nitrite ions formed by hydrolysis of the inhibitor oxidize iron, forming a monomolecular FeO layer; the liberated dicyclohexylamine ions bind the acid gases penetrating to the metal.

However, this account of the mechanism completely disregards the electrochemical processes involved in atmospheric corrosion, and does not explain the mechanism of protective action of DICHAN in solution, where corrosion is certainly electrochemical. It was therefore of interest to study the electrochemical behavior of steel in DICHAN solutions.

The experiments were performed with specimens of carbon steel containing 1.2% carbon. The electrolyte was town water of total hardness 180 mg/liter, containing 22 mg chlorides and 46 mg sulfate per liter. The time variations of the potential of steel in solutions containing different amounts of DICHAN, and the nature of the polarization in these solutions, were studied.

Figure 1 shows that in solutions of high DICHAN concentrations (20-40 g/liter) the potential of steel changes rapidly and stably in the positive direction. At lower DICHAN concentrations (5-10 g/liter) activation of the steel as the result of dissolution of its natural oxide film evidently prevails for 20-30 minutes over the passivating effect of DICHAN. As the exposure time increases, the passivating action of DICHAN leads to stable positive values of the potential.

The second group of curves, characterized by relatively small changes of potential in time, correspond to DICHAN concentrations from 0.45 to 2.5 g/liter. At these DICHAN concentrations the potential of steel fluctuates in the range from -30 to -190 mv (as compared with +180 to +210 mv at higher concentrations), and a tendency to further ennoblement is observed in the solution containing 0.45 g DICHAN per liter. A lower DICHAN concentration (0.31 g/liter) has little effect on the course of the potential variations as compared with pure town water. The stable potentials in this solution are only 50 mv on the positive side of the potential of steel in town water. The potential of steel varies similarly in saturated dicyclohexylamine solution, the concentration of which is 1.6 g/liter.

It should be noted that the specimens were corroded in all DICHAN solutions containing less than 2.5 g/liter, and in saturated dicyclohexylamine solution.

* Original Russian pagination. See C. B. Translation.

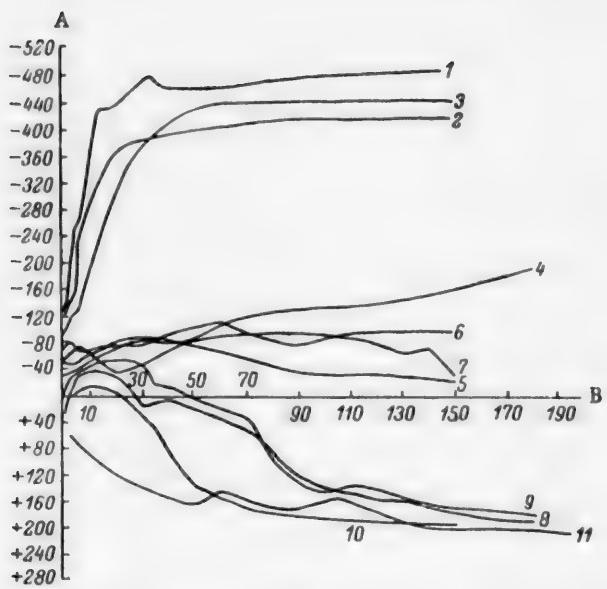


Fig. 1. Time variations of the potential of a steel specimen in various solutions. A) Potential (mv); B) time (minutes).
Solutions: 1) town water, 2) water saturated with dicyclohexylamine. Solutions of DICHAN of concentrations
(g/liter): 3) 0.31, 4) 0.45, 5) 0.62, 6) 1.25, 7) 2.5,
8) 5.0, 9) 10, 10) 20, 11) 40.0.

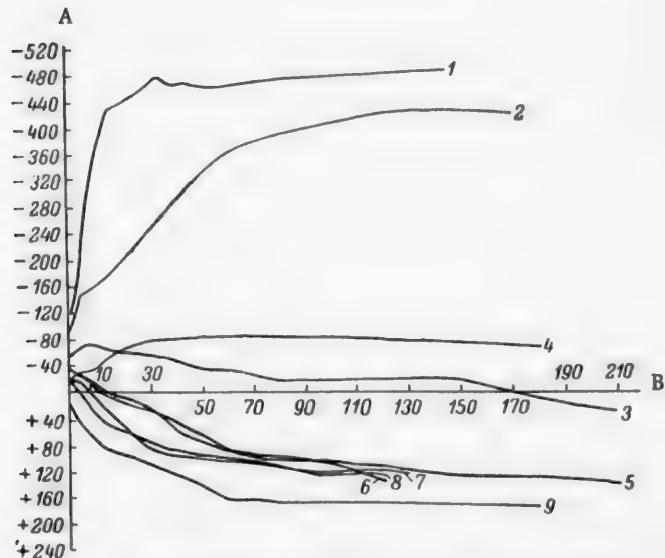


Fig. 2. Time variations of the potential of a steel specimen in various solutions. A) Potential (mv); B) time (minutes).
Solutions: 1) town water, Sodium nitrite solutions (g/liter):
2) 0.09, 3) 0.18, 4) 0.37, 5) 0.75, 6) 1.5, 7) 3.08,
8) 6.0, 9) 12.0.

Analogous results were obtained for the time variations of the potential of steel in sodium nitrite solutions (Fig. 2) containing the same amounts of nitrite ions as the DICHAN solutions used earlier.

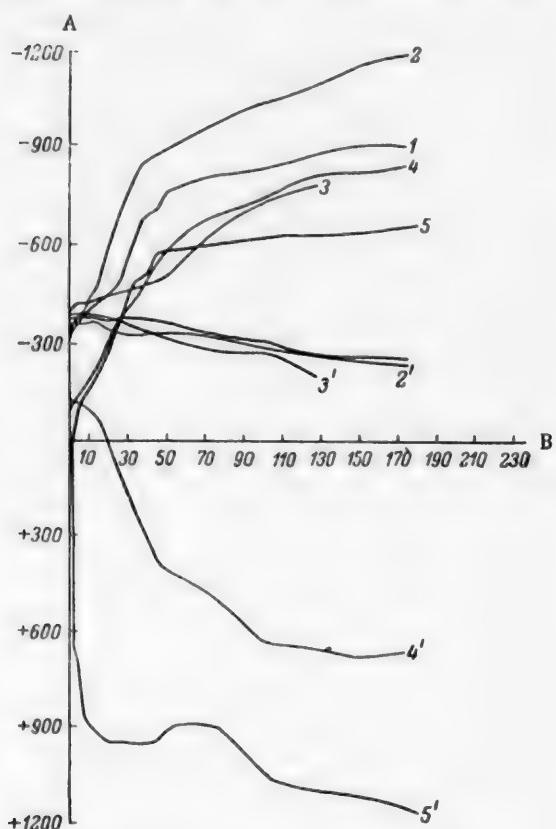


Fig. 3. Polarization curves for steel specimens. A) Potential (mv); B) current density (amp/cm²).

1) Town water, 2) water saturated with dicyclohexylamine. Solutions of DICHAN of concentrations (g/liter): 3) 0.45, 4) 2.5, 5) 40.0.

cation) is virtually the same (if the differences of equilibrium potential are taken into account), and is only slightly higher than in town water. Therefore, the influence of dicyclohexylamine is very slight on the cathode process also.

All these results indicate that the protective action of DICHAN is due only to the presence of nitrite ions. Since atmospheric corrosion occurs in a more or less thin film of moisture formed in the metal surface, the protective action of DICHAN against atmospheric corrosion may also be attributed to the presence of nitrite ions. If so, the role of dicyclohexylamine is to give rise to cations which form a volatile compound, evaporating even at room temperature, with nitrite ions. It follows that dicyclohexylamine ions, having no protective effects in themselves, may be replaced by any other cations which can form nitrites of high enough vapor pressure.

With regard to neutralization of acid gases in the atmosphere by dicyclohexylamine, in view of the absence of any specific protective action of dicyclohexylamine such neutralization may be effected by any other cations.

Comparison of the curves in Fig. 2 with those in Fig. 1 shows that the time variations of the potential of steel in relation to the inhibitor concentration are the same for DICHAN solutions and for sodium nitrite solutions, with small differences in the absolute values of the potentials. Since the concentrations of nitrite ions in the corresponding solutions were equal, this agreement shows that the nature of the variations of potential with time is primarily determined by the influence of the nitrite ion and not of the particular cation.

Polarization curves (Fig. 3) were determined for steel in DICHAN solutions containing 0.45, 2.5, and 40 g/liter, in saturated dicyclohexylamine solution, and in town water.

It is seen in Fig. 3 that in a solution containing 40 g DICHAN per liter, which completely protects the steel from corrosion, slight anodic polarization shifts the potential sharply in the positive direction. In a DICHAN solution containing 2.5 g/liter, where some corrosion occurs, anodic polarization results in a much smaller shift of potential. In saturated dicyclohexylamine solution and in a solution containing 0.45 g DICHAN per liter the anodic polarization curve is virtually the same as the anodic polarization curve for town water. This shows that dicyclohexylamine does not influence the anode process, and that the shift of potential during anodic polarization in solutions of high DICHAN concentrations is due to the action of nitrite ions.

The cathodic polarization in solutions of different contents of dicyclohexylamine (as the

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REACTION OF HUMIC ACIDS WITH DIMEDONE

T. A. Kukharenko and L. N. Ekaterinina

It is known that humic acid molecules contain carbonyl groups. Their presence has been demonstrated by many workers, by means of the reaction with phenylhydrazine and its derivatives, and the reaction with hydroxylamine. However, the question of the character of the carbonyl groups has been studied little. According to Fuchs, the carbonyl groups in humic acids are each linked to two radicals, i.e., they are ketonic in character [1].

We found that humic acids of peats and coals react with dimedone which is a specific reagent for aldehydes. The reaction of dimedone with aldehydes yields condensation products which are precipitated from the reaction mixture [2]. Aldehyde groups may be determined gravimetrically by isolation of the condensation product, or volumetrically from the required amount of dimedone which can react as a monobasic acid.

The reaction was carried out in aqueous alcohol, heated on a water bath [3], and at room temperature [4, 5]. In most cases the results obtained by the two methods were in good agreement. However, in some instances colored products soluble in aqueous alcohol formed on heating, so that it was impossible to determine dimedone accurately after the condensation product had been filtered off. We therefore used Rozenberg's method for determination of aldehyde groups at room temperature [5].

Carbonyl Group Contents of Humic Acids from Different Coals,
Determined by the Phenylhydrazine and Dimedone Reactions

Source of humic acids	Contents (meq/g)	
	carbonyl groups, by phenylhydrazine reaction	aldehyde groups, by dimedone reaction
"Galician moss" peat	1.47	0.75
Aleksandriya brown coal	1.96	0.24
Weathered coals from Kuzbass pits:		
"Maneikha" (near roof)	1.80	0.35
the same (3 m from roof)	1.36	0.67
"Severnaya" (0.15 m from roof)	—	0.37
the same (1.05 m from roof)	2.30	1.36
"Baidaevskaya"	2.39	1.32

A weighed sample of humic acids (about 0.1 g) and 10 ml of 1:1 aqueous alcohol was put in a flask fitted with a ground-glass stopper. To the suspension 10 ml of 0.1 N dimedone solution in the same solvent mixture was added. The reaction mixture was shaken and left to stand 48 hours at room temperature. The precipitate

was then filtered off and washed with alcohol - water mixture; the filtrate and wash liquors were collected in a 100 ml measuring flask. 10 ml portions were then taken and titrated with 0.1 N caustic potash solution. The aldehyde group content was calculated from the difference between the original amount of dimedone and the amount found after the reaction, and expressed in milliequivalents per g of humic acids.

The aldehyde group contents of humic acids from peat and different coals, determined by this method, are given in the table. It is seen that the humic acids contain aldehyde groups. The aldehyde group contents of different samples vary from 0.24 to 1.36 meq/g. A very interesting fact is that humic acids from coals differing in their degree of weathering also differ in aldehyde group contents. Humic acids of more weathered coals have lower aldehyde group contents. The results of the phenylhydrazine reaction show that the aldehyde group contents of humic acids are lower than the total carbonyl group contents; this indicates the presence of ketone groups.

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SYNTHESIS OF A MOLECULAR COMPOUND OF DI(TRIETHYLSILOXY)LEAD AND LEAD HYDROXIDE, AND ITS REACTION WITH TITANIUM TETRACHLORIDE

K. A. Andrianov, A. A. Zhdanov, and E. A. Kashutina

In work on new methods for synthesis of trialkylsiloxy metals of the general formula $(R_3SiO)_nMe$ it was necessary to synthesize tetrakis(triethylsiloxy)titanium by the reaction



The preparation of di(trimethylsiloxy)lead by the action of lead oxide on trimethylsilanol is described in [1]:



However, analysis of the compound so obtained for lead showed a considerable discrepancy between the theoretical and experimental results (calculated, Pb 53.7%; found, Pb 59.1%). These results suggested that the reaction of trimethylsilanol and lead oxide in reality proceeds according to another equation. The reaction of lead hydroxide and triethylsilanol should give di(trimethylsiloxy)lead. However, it was found by investigation

that when triethylsilanol reacts with lead hydroxide a compound is formed from two molecules of di(triethylsiloxy) lead and one molecule of lead hydroxide:



This compound is obtained in a high yield.

A study of the reaction of this compound with titanium tetrachloride led to a new method for synthesis of tetrakis(triethylsiloxy)titanium, a compound already described in [2, 3]. The reaction proceeds according to the scheme



EXPERIMENTAL

Molecular compound of di(triethylsiloxy) lead with lead hydroxide. A three-necked flask fitted with a stirrer, reflux condenser with a calcium chloride tube, and a thermometer, contained 68 g (0.28 mole) of lead hydroxide, 50 g of freshly calcined sodium sulfate, and a solution of 50 g (0.38 mole) of freshly distilled triethylsilanol in 130 ml of dry benzene. The mixture was stirred at 40–50° for 12 hours. At the end of the reaction (when the solution became clear) sodium sulfate was filtered off, and benzene was removed from the filtrate under vacuum (on a water bath). The substance remaining in the distillation flask was pressed out rapidly on a Buchner funnel; the yield was 80 g (73% of the theoretical) of a white crystalline substance which decomposes before melting when heated.

Found %: C 23.55, 23.43; H 5.23, 5.10; Pb 51.23, 51.97; M* 1030. $\text{C}_{24}\text{H}_{62}\text{O}_6\text{Si}_4\text{Pb}_3$. Calculated %: C 24.40; H 5.28; Pb 52.65; M 1180.

Tetrakis(triethylsiloxy)titanium. 58 g (0.05 mole) of the di(triethylsiloxy) lead derivative was dissolved in 100 ml of dry benzene in a three-necked flask fitted with a stirrer, a reflux condenser with a calcium chloride tube, and a dropping funnel. A solution of 14.4 g (0.075 mole) of titanium tetrachloride in 50 ml of dry benzene was added dropwise to this solution during 1.5 hours. The temperature rose to 40°. When the benzene solution of titanium tetrachloride had been added, the reaction mixture was stirred for a further 30 minutes and left overnight. The precipitate was then filtered off, benzene was distilled from the filtrate, and the residue was distilled under vacuum. The yield was 14 g (50% of the theoretical) of tetrakis(triethylsiloxy) silane of b. p. 176–178° (2–3 mm), m. p. 96°.

Found %: C 50.72, 50.58; H 10.68, 10.77; Ti 9.10, 9.08. $\text{C}_{24}\text{H}_{60}\text{O}_4\text{Si}_4\text{Ti}$. Calculated %: C 50.32; H 10.66; Ti 8.36.

The precipitate was filtered off, dried, and washed with hot water until lead chloride was removed completely (34 g of lead chloride was obtained). The undissolved portion of the precipitate [$\text{Pb}(\text{OH})_2 + \text{Ti}(\text{OH})_4$] was treated with hot hydrochloric acid to dissolve lead hydroxide. The insoluble residue [$\text{Ti}(\text{OH})_4$] was washed with water, dried, and weighed. The weight of the residue was 1 g. It follows from the above that the lead hydroxide present in the molecular compound with di(triethylsiloxy) lead reacts rather slowly with titanium tetrachloride.

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* Determined cryoscopically in benzene.

** See C.B. Translation.

SYNTHESIS OF TRI(DIMETHYLPHENYL-p-CRESYL) PHOSPHATE

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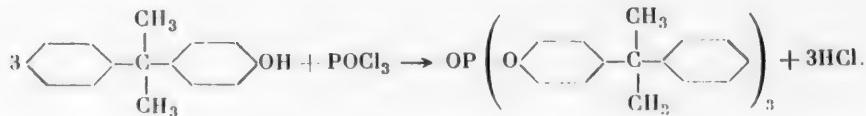
Laboratory of the Chair of Organic Synthesis Technology, the Kazan' Institute of Chemical Technology

Phenyl esters of phosphoric and phosphorous acids and their various derivatives have long been known and are extensively used in industry as plasticizers, antioxidants, insecticides and fungicides, etc. [1-4]. These compounds include triphenyl phosphate, tricresyl phosphate, trichlorophenyl phosphate, trinitrophenyl phosphate, etc.

The synthesis and properties of polyphenyl derivatives of phosphorus acids have not been described in the literature, and therefore synthesis of dimethylphenyl-p-cresyl phosphate is of great theoretical and practical interest.

We have found that this synthesis proceeds with ease, differing very little from the synthesis of tricresyl phosphate, with formation of tri(dimethylphenyl-p-cresyl) phosphate.

The formation of tri(dimethylphenyl-p-cresyl) phosphate may be represented as follows:



Magnesium chloride is a good catalyst for this reaction. The synthesis is performed at relatively high temperatures, 120-170°. The high boiling point and compatibility with a number of polymers make this compound promising for industrial use.

EXPERIMENTAL

Into a three-necked flask fitted with a thermometer, dropping funnel, stirrer, and reflux condenser there was put 51.9 g of dimethylphenyl-p-cresol, which was melted at 68-70°. Magnesium chloride catalyst (0.5% on the weight of the phenol) was added to the melted dimethylphenyl-p-cresol, 14 g of phosphorus oxychloride was then added from a dropping funnel with stirring at 80°. The evolving hydrogen chloride was absorbed in water. The temperature of the reaction mass was raised gradually to 170° during ten hours, and dry carbon dioxide was then blown through the reaction mass to remove hydrogen chloride and residual phosphorus oxychloride.

The reaction mass can itself be used as a plasticizer. To isolate pure tri(dimethylphenyl-p-cresyl) phosphate, the reaction mixture was distilled under vacuum. The compound has exceptional chemical stability.

The following fractions were obtained (at 1 mm): 1) 160-290°, 2) 330-350°, 3) 370-400°, 4) residue in still, 65.9 g.

Analysis of the 3rd fraction gave the following results:

Found %: P 4.92; C 78.09; H 7.12; M 687. Calculated %: P 4.45; C 79.41; H 6.62; M 680.

The yield of tri(dimethylphenyl-p-cresyl) phosphate was 90%.

After removal of hydrogen chloride and residual phosphorus oxychloride from the reaction mixture the latter can be distilled under vacuum without neutralization of the added catalyst; the yield of the phosphate therefore reaches 90-95%.

Tri(dimethylphenyl-p-cresyl) phosphate has a high boiling point. It boils without decomposition at 390-400° (0.1 mm). Its distinctive peculiarity is that it crystallizes with difficulty, and consists of an undercooled highly viscous transparent yellowish liquid. After a second distillation the liquid crystallizes during slow cooling. The

crystalline product melts at 142°. Tri(dimethylphenyl-p-cresyl) phosphate is insoluble in ether and readily soluble in tricresyl phosphate, triphenyl phosphate, benzene, butyl acetate, and acetone. Tri(dimethylphenyl-p-cresyl) phosphate recrystallizes well from ethyl alcohol. Tri(dimethylphenyl-p-cresyl) phosphate plasticizes polyvinyl chloride, nitrocellulose, and other polymers, making them self-extinguishing. It can also be used in conjunction with other plasticizers.

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INVESTIGATION OF THE PROTEINS OF WINTER RYE

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A new variety of winter rye, "Voronezh SKhI" (Voronezh Agricultural Institute), was taken from the 1952 and 1955 crops raised at the Field Experimental Station of the Voronezh Agricultural Institute; rye of "Lisitsyna" variety from the same station was taken for comparison.

All the samples were ground. The following were determined in the flour: hygroscopic water; ash; fat; total, protein, and nonprotein nitrogen (by the usual methods); the results were expressed in percentages of the bone-dry substance (Table 1); the protein fractions were then determined [1-4]. For these determinations 10 g of each flour sample was taken and treated successively with a 10-fold quantity of water, 10% NaCl solution, 0.25% NaOH solution, and 70% alcohol. The residues after the salt and alkali extractions were washed free of NaCl and NaOH; the wash waters were added to the corresponding extracts.

Each extraction was performed twice for 2 hours and 1 hour, respectively with shaking, and the extracts were combined.

All the extracts were measured; 50 ml of solution was taken from each into a Kjeldahl flask and burned with subsequent distillation of ammonia. The amounts of nitrogen found gave the contents of the respective protein fractions. The results of nitrogen determinations for the individual fractions were calculated as percentages on the dry substance and total and protein nitrogen (Table 2).

The data in Tables 1 and 2 show that "Voronezh SKhI", a variety new in the Central Black Sea Belt of the USSR is even superior to the "Lisitsyna" variety in total nitrogen content and in contents of individual protein fractions.

TABLE 1
Results of Flour Analyses

	Rye variety			
	Voronezh SKhI		Lisitsyna	
	1952	1955	1952	1955
Moisture (%)	11.16	12.46	11.62	12.81
Ash (%)	1.76	1.99	2.00	2.22
Fat (%)	1.67	1.91	1.90	1.81
Nitrogen (%):				
total	2.21	2.48	2.17	1.98
protein	1.88	1.99	1.68	1.64
nonprotein	0.33	0.49	0.49	0.34
Yield (centners/hectare) air-dry	26.3	37.9	22.9	34.8

TABLE 2
Results of Nitrogen Determinations in Individual Protein Fractions

Substance	Rye variety											
	Voronezh SKhI, 1952 crop			Voronezh SKhI, 1955 crop			Lisitsyna, 1952 crop			Lisitsyna, 1955 crop		
	% on dry flour	% of total nitrogen	% of protein nitrogen	% on dry flour	% of total nitrogen	% of protein nitrogen	% on dry flour	% of total nitrogen	% of protein nitrogen	% on dry flour	% of total nitrogen	% of protein nitrogen
Albumin	0.49	22.17	26.06	0.34	13.71	17.09	0.37	17.05	22.02	0.46	23.23	28.05
Globulin	0.54	24.43	28.72	0.79	31.85	39.70	0.56	25.81	33.33	0.45	22.73	27.44
Gliadin	0.18	8.14	9.57	0.14	5.65	7.04	0.10	4.61	5.95	0.18	9.09	10.98
Glutenin	0.46	20.81	24.47	0.65	26.21	32.66	0.31	14.29	18.45	0.27	13.64	16.46

In view of the yield and grain quality it may be claimed that the "Voronezh SKhI" rye variety is the most promising, and may play a significant role in solution of the grain problem of our country.

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INVESTIGATION OF THE STRUCTURAL CHARACTERISTICS AND CHEMICAL CONVERSIONS OF CARBAZOLE AND SOME OF ITS DERIVATIVES*

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Dyes derived from carbazole, made both synthetically and from coal-tar carbazole, are now used fairly widely abroad because of their good qualities: fastness to laundering and light. These include the sulfur Hydron dyes [1-3], dyes based on p-hydroxycarbazole carboxylic acids [4], etc.

Carbazole derivatives which are difficult to prepare are often used as intermediates in the production of these dyes.

In the paper by Ruff and Stein [5] on the properties and reactions of 3-diazocarbazole it is stated that azo dyes derived from 3-diazocarbazole, despite their good fastness to light, cannot be of practical interest as they give similar brownish-violet dull shades.

In view of the present availability of a variety of azoic coupling components, we have attempted to synthesize new azo dyes from 3-diazocarbazole, in order either to demonstrate the unsuitability of these dyes for practical purposes or to show that they may be used.

We synthesized 8 substantive dyes by the coupling of 3-diazocarbazole with 1,8-acetylaminonaphthol-3,6-disulfonic acid, 1,8-aminonaphthol-3,6-disulfonic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, 1-phenylnaphthylamino-8-sulfonic acid, 1-p-tolylnaphthylamine-8-sulfonic acid, 1,6- and 1,7-naphthylamino-sulfonic acids, and the Scarlet acid; 3 dyes Azotols A, ANF, and phenylmethylpyrazolone were made in the fiber by the ice-dyeing method. The 3-aminocarbazole used for preparation of the diazo compound was obtained by a modification of the method described by Éikman et al. [6] in a good yield (85% of the theoretical yield calculated on the carbazole).

It was found that 3-diazocarbazole can be used to prepare dyes which color various fabrics in a variety of shades, from black to golden yellow, of pure and bright hues. Most of the dyes dissolve fairly well in water, and dye rayon and silk, and tannin-mordanted cotton. All the substantive dyes have particular affinity for Capron fiber. The dyeings are in most instances very fast to washing, rubbing, and light.

EXPERIMENTAL

Preparation of 3-diazocarbazole. 1.82 g (0.01 mole) of 3-aminocarbazole was ground in a mortar with 8 ml of 12% hydrochloric acid solution, the mixture was transferred to a porcelain beaker, 120 ml of ice water was added, and sodium nitrite solution (0.78 g in 2-3 ml of water) was added to it at once with vigorous stirring. The reaction mass was stirred for 40 minutes and filtered. The tea-colored solution was used for coupling (the reaction is performed in the dark because 3-diazocarbazole decomposes on exposure to light).

Preparation of substantive dyes. The azoic coupling components were dissolved on warming in 20-50 ml of water with addition of alkaline agents, the solution was rapidly cooled in ice down to -5°, and an equimolecular amount of 3-diazocarbazole solution was added with vigorous stirring; an additional amount of alkaline condensing agent was also added. The reaction mass was stirred in the cold, a small amount of common salt was added at room temperature during 8-12 hours, the mixture was kept in the cold for 24 hours, and the dye was filtered off, dried, and ground. The percentage content of the dye was determined by titration with stannous chloride solution.

The results are given in Table 1.

* Communication III in the series on azo dyes—derivatives of 3-diazocarbazole.

TABLE I
Results of Experiments on Preparation of Substantive Dyes

Azoic coupling components	Alkaline agents		Yield (% of theoretical)	Dye content (%)	Fibers dyed	Properties of dyeings	
	for dissolving	for condensation				color	fastness
1,8-Acetylaminonaphthalen-3,8-disulfonic acid	Na ₂ CO ₃	NH ₄ OH concentrated	93	72	Silk, rayon, cotton, Capron	Intense bluish-red	High fastness to washing, rubbing, and light
1,8-Aminonaphthalen-3,6-disulfonic acid	Na ₂ CO ₃	NaOH, 35% solution	86	74	Silk, rayon, cotton, Capron	Light bluish-red	High fastness to washing, rubbing, and light
1,8-Dihydroxynaphthalene-3,6-disulfonic acid	CH ₃ COONa	Na ₂ CO ₃	84	66	Silk, rayon, cotton, Capron	Pale blue	Low fastness to washing and rubbing
1-Phenylnaphthylamino-8-sulfonic acid	Na ₂ CO ₃	CH ₃ COONa	88	62	Rayon	Blue	Fast to washing and rubbing
1-P-tolylnaphthylamino-8-sulfonic acid	Na ₂ CO ₃	CH ₃ COONa	89	65	Silk, Capron	Rose	Moderate fastness to washing and rubbing
1,6-Naphthylamino-sulfonic acid	Na ₂ CO ₃	CH ₃ COOH	86	71	Rayon, cotton	Brownish-red	High fastness
1,7-Naphthylamino-sulfonic acid	Na ₂ CO ₃	CH ₃ COOK	92	68	Silk, Capron	Red	Moderate fastness
Scarlet acid	Na ₂ CO ₃	Na ₂ CO ₃ 25% solution	89	75	Rayon, cotton, silk, Capron	Orange	High fastness to washing, rubbing and light
						Golden orange	High fastness to washing, rubbing and light
						Pale brown with a golden tinge	Moderate fastness to washing and rubbing
						Reddish-blue	High fastness to light

Formation of dyes on the fiber. The diazo solution prepared as described above was diluted with water (50 ml of ice water to 100 ml of diazo solution), sodium acetate was added, the pH was brought to 7.5-8, and the solution was applied to padded fabrics.

Previously-soaked fabric samples were padded in aqueous solutions of the azoic coupling components containing small amounts of sodium carbonate or acetate. The results are given in Table 2.

TABLE 2
Results of Experiments on Formation of Dyes on the Fiber

Azoic coupling component	Fiber dyed*	Properties of dyeings	
		color	fastness
Phenylmethyl-pyrazolone	Cotton, rayon, silk	Orange	Moderate to washing and rubbing
Azotol A	Cotton, rayon, silk	Black with bluish tinge	High to washing, rubbing, and light
Azotol ANF	Cotton, rayon, silk	Black with brownish tinge	High to washing, rubbing, and light

* Capron fibers are not dyed.

SUMMARY

The 11 new and fast azo dyes based on carbazole (contained in large amounts in coal tar and little used in industry at present) prepared by a simple and convenient method have high affinity for caprolactam fibers.

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ALL-UNION CONFERENCE ON TRACE ELEMENTS

Representatives of more than 70 different scientific research institutions from all the 15 Union Republics were present in Baku during the second half of April at the Third All-Union Conference on Trace Elements, convened by the Academy of Sciences, USSR, jointly with the Academy of Sciences, Azerbaijan SSR.

The science of trace elements, which has developed during the past 25-30 years, has the widest potentialities, from sharp increases in the yields of agricultural crops and increased productivity in stock breeding to utilization of these chemical substances in medicine.

The role of dozens of chemical elements, which between them do not exceed 0.5% of the weight of animal and plant organisms, long remained obscure. It is only gradually that the causes of the influence of compounds of manganese, boron, copper, and later zinc, cobalt, molybdenum, iodine, and many others have begun to be determined. Despite the fact that only 10^{-3} to $10^{-12}\%$ of each of these trace elements is present in the organism, life processes are impossible without them.

Trace elements are contained in many enzymes, vitamins, proteins, and hormones and have an active influence on carbohydrate and protein metabolism in organisms, on enzyme activity, vitamin synthesis, and a number of other most important biochemical processes. As the result of these effects, utilization of trace elements may increase not only the yields of all agricultural crops, but also the drought and frost resistance of plants, resistance to various diseases, it may shorten ripening times considerably and improve the quality of agricultural products. Addition of trace elements to cattle fodder improves the general condition of the animals and increases their meat and milk output.

The world literature is being increased annually by numerous new publications on studies of trace elements by biologists, chemists, agronomists, doctors, and many others.

However, many aspects of the mechanism of trace -element action are still not understood, and further work in this field may lead to important discoveries in relation to life processes taking place in organisms. The role of trace elements in many of the most important life processes was discussed in a number of papers presented at the Conference.

In the paper by the President of the Academy of Sciences Latvian SSR, Corresponding Member (AN SSSR) Ya. V. Peive, on the relationship between soil conditions and the action of trace elements on plants, emphasis was laid on the fact that the effectiveness of trace elements depends not only on their presence in the soil in assimilable form, but also on other elements of plant nutrition, on the reaction of the medium, on the dynamics of microbiological and soil-chemical processes, and on a number of other soil properties. The maximum effect can be obtained only by differentiated, nonstereotyped use of trace elements. At the same time Ya. P. Peive justly pointed out that trace elements are being applied only over 0.2-0.3% of the arable area of the country, which is quite inadmissible.

In the Ukraine, in Latvia, Belorussia, Georgia, Azerbaijan, and in certain regions of the RSFSR, important investigations have been carried out on the contents of trace elements in the soil, in forms accessible to plants (by P. A. Vlasyuk, Sh. F. Chanishvili, V. V. Akimtsev, G. A. Aliev, A. N. Gyul'akhmedov, D. P. Malyuga, N. P. Shergin, A. L. Makarova, R. S. Osokina, A. A. Alekseev, and M. S. Dzhurko, Ya. V. Peive and N. N. Ivanova, M. V. Katalymov and S. I. Ryabova, V. A. Chernov, and others). Development of convenient methods of chemical soil analysis is required for more extensive coverage of various fields by such researches. Several methods, developed in the Academy of Sciences Latvian SSR (Ya. V. Peive), for quantitative determination of trace elements in soil, applicable under field conditions, were demonstrated at the Conference. A compact field laboratory has been constructed, which can be used for carrying out analyses directly in any collective farm.

Numerous papers demonstrated the high effectiveness of the trace elements manganese, boron, copper, molybdenum, cobalt, and zinc, and also less-studied compounds of nickel, aluminum, vanadium, and chromium, in relation to a great variety of agricultural crops (P. A. Vlasyuk, G. A. Aliev, O. K. Kedrov-Zikhman, M. Ya. Shkol'nik, M. G. Abutalybov, D. M. Guseinov, A. V. Peterburgskii, E. I. Ratner, S. S. Abaeva, V. V. Yakovleva, A. P. Shcherbakov, O. K. Dobrolyubskii, and others). Utilization of various industrial wastes, such as manganese sludges, pyrite cinders, oil-well waters, etc. is particularly important.

One important task for the chemical industry is the production of sufficient amounts of various trace-element fertilizers, which are so necessary for agriculture. The range of trace-element fertilizers now being produced is quite inadequate, both in quantity and in quality as compared with the requirements. At the present time our industry is producing only one type of boron fertilizer, boron magnesium sulfate, and that only in very small amounts. However, as M. V. Katalymov pointed out in his paper, a technological and chemical study of various forms of boron fertilizers, conducted in the Scientific Research Institute for Fertilizers and Insectofungicides (NIUIF), showed that the most promising fertilizers are ordinary and double borated superphosphates, boric acid, borated datolite fertilizer, and precipitated magnesium borate.

A sharp increase is necessary in the production of various fertilizers containing not only boron or manganese, but also copper, zinc, molybdenum, cobalt, and a number of other trace elements. At the present time various combined fertilizers containing the macro and trace elements simultaneously are being produced in many foreign countries, including the Peoples' Democracies (Czechoslovakia, Democratic German Republic). Molybdenum fertilizers are used extensively and with success in the United States, New Zealand, Australia, and other countries; and zinc fertilizers, which are especially effective for tung trees, grape vines, and various fruits, are used in the United States, England, France, and Greece.

For treatment of seeds before sowing and for foliar feeding it is not necessary to use reagents of analytical or even chemically pure grades; it is quite possible to use technical salts, which are much cheaper. The output of analytical reagents does not allow for the needs of agriculture, while the latter type of reagent is not produced by the chemical industry at all. There should be no difficulty in organizing the production of, say, technical zinc sulfate or manganese sulfate.

Recently new ceramic fertilizers (frits) have come into use; these are a special type of glass melts containing various macro and trace elements. Questions of frit utilization were considered in the papers by Ya. V. Peive and R. S. Rin'ke, P. A. Vlasyuk and M. S. Darmenko, A. P. Shcherbakov and T. I. Kuraktanova, and N. I. Baglykov. The advantage of using frits rather than trace elements in the usual manner is that they can be introduced once in several years, with the simultaneous introduction of several trace elements. Trace elements are not leached out of frits by water, but are slowly assimilated as needed by the plant organisms in contact with the root systems and by exchange reactions. It should be noted that because of their low solubility frits are not harmful to plants even when introduced in excess.

The Conference delegates were greatly interested by the paper of one of the most eminent specialists in the field of trace elements, M. Ya. Shkol'nik (The V. L. Komarov Botanical Institute, Academy of Sciences, USSR), on physiological and biochemical investigations. Important discoveries in the field of enzyme and vitamin chemistry, and new facts on the infinite variety of organomineral complexes in the organism, demonstrate that trace elements play an important role in life processes.

The recent discovery that a number of metal compounds participate in flavoprotein catalysis is of special importance.

The Conference included many interesting papers demonstrating the importance of various trace elements in photosynthesis processes, carbohydrate and protein metabolism, enzyme activity, etc. The importance of trace elements in oxidation-reduction reactions in the living organism is particularly great, as the direction of such processes depends on the proportions of mineral elements. New data have been obtained on the participation of boron, manganese, and molybdenum compounds in fertilization and fruit formation, and on the influence of trace elements on the drought and salt resistance of plants. Interesting facts have been discovered concerning trace-element requirements and mineral deficiency in relation to temperature, humidity, light intensity, proportions of mineral elements, etc.

S. M. Manskaya and T. V. Drozdova (the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry) reported on the significance of natural organic compounds in concentration of trace elements. Thus, migration of copper is possible in natural processes, with formation of various soluble compounds with humic acids (dependent on the pH of the medium), and also concentration of copper with formation of insoluble humates and fulvates.

L. K. Ostrovskaya showed in a very interesting communication that the demand of plants for copper fertilizers increases with increase of the level of nitrogen feeding. Protein synthesis is retarded if there is a deficiency

of copper compounds in feeding with ammoniacal nitrogen, but there is no appreciable influence on the synthesis of such nitrogen compounds as amino acids, bases, and amides. P. A. Vlasyuk and Z. M. Klimovitskaya showed that the retardation of plant growth and development in boron deficiency is associated with far-reaching disturbances of oxidation-reduction processes.

Inner-complex compounds (chelate compounds) play an important part in biochemical processes. A number of enzymes (such as cytochrome catalase, etc.) form "chelate structures" with trace elements; in other enzymes metal ions are in equilibrium with organic molecules acting as chelates. Any substance which precipitates or binds a metal ion contained in an enzyme would remove it from the enzyme and therefore suppress its activity. It is regrettable that, apart from the papers by M. Ya. Shkol'nik and Ya. V. Peive, there were no communications on chelates, because the practical importance of these inner-complex compounds is very great.

Ya. V. Peive and N. N. Ivanova, and also Yu. N. Dobritskaya, reported on methods of molybdenum determination in soils and plants, and M. V. Katalymov and S. I. Ryabova described a method for determination of reactive boron. A. N. Gyul'akhmedov reported on a rapid method for determination of total manganese, copper, and cobalt in carbonate soils. Moreover, the last-named speaker presented several interesting communications on the use of tagged atoms for studies of the absorption of trace elements by soil, their absorption by plants, and investigation of the influence of trace elements on the salt resistance of the cotton plant.

Further work is needed on accurate and rapid chemical methods for determination of trace elements in plant and animal materials.

Many theoretical questions of the role of trace elements are still inadequately studied. There have been a number of attempts to classify the elements by their roles in the biosphere. The views of L. Ya. Levanidov are of interest in this connection; he suggested the formation of a group of variable-valence elements which do not form volatile compounds during weathering and which have high oxidation-reduction potentials. L. Ya. Levanidov considered the role of the trace element manganese in the biosynthesis by plants of compounds with low oxidation-reduction potentials. A. P. Shcherbakov considered various macro and trace elements in an important attempt to examine physiological antagonism, synergism, and additivity. O. K. Dobrolyubskii investigated the influence of certain little-studied trace elements (chromium, nickel, cobalt, cadmium, mercury, and others) and correlated their role with their positions in definite groups of D. I. Mendeleev's periodic system.

The entire surface of the earth consists of zones differing in chemical composition. It was pointed out in a very important paper by V. V. Koval'skii that there are regions or areas (often extensive) within which there are observed very appreciable and characteristic reactions of organisms to excess or deficiency of macro and trace elements. These biogeochemical regions, the science of which has been developed by Academicians V. I. Vernadskii and A. P. Vinogradov, are more widely distributed than might have been supposed even quite recently.

The whole history of the earth is associated with accumulation of compounds of definite chemical elements. It is known, in particular, that there is a deficiency of cobalt, copper, and iodine compounds in the nonchernozem zone of podzolic turf soils which girds the land mass of the Northern hemisphere. In the biogeochemical regions of the nonchernozem zone there are many endemic diseases—cobalt deficiency, B_{12} avitaminosis, while among plants there is the disease known as "lodging," and failure to ripen, caused by copper deficiency and disturbance of the functions of oxidation-reduction enzymes.

Thus, a new science—chemical geography—has arisen from biogeochemistry, which is concerned with migration of atoms and geochemical processes taking place under the influence of organisms in the biosphere.

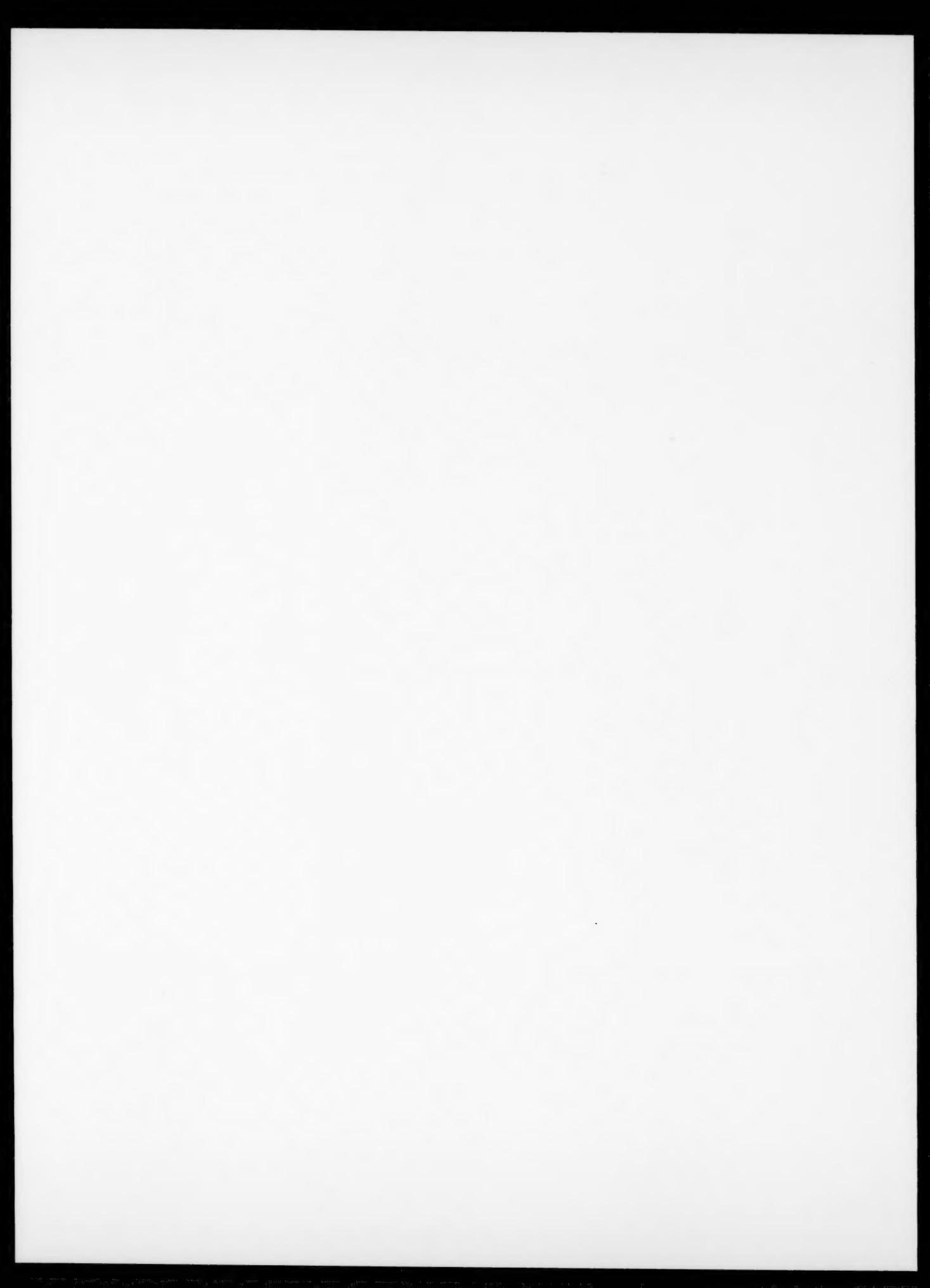
Valuable investigations demonstrating the favorable effects of trace elements on farm animals were reported in numerous papers (Ya. M. Berzin', N. I. Zaderii, F. A. Petrov, and others). In a number of other papers there were considered biochemical processes taking place in animal organisms under the influence of trace elements, and causes of action of these elements (N. P. Shergin, F. Ya. Berenshtein, A. D. Gololobov, Ya. A. Babin, and others).

In one of the most interesting papers at the Conference, given by A. O. Voinar, it was shown that trace elements have a great influence on the human organism as well as animals. It is likewise difficult to overestimate the significance of trace elements in medicine. There were some dozens of papers on this subject even at this Conference, demonstrating the presence of certain trace elements in the organs of human embryos, in the blood of patients suffering from endemic goiter (V. A. Leonov), in the tissues of diseased thyroid glands

(V. M. Shostkov), in malignant tumors during their growth (E. N. Ivanova). Other subjects considered were the diurnal variations of trace elements in the blood (E. V. Sabadash), copper metabolism in pregnancy (M. G. Mirzakarimov), reactions of the animal organism to introduction of trace elements (A. I. Venchikov), the contents of certain trace elements in acute leukemias (R. G. Kapran), etc. Thus, trace elements can be both foes and friends of man. The important thing is to direct life processes along the desired course with their aid.

O. K. Dobrolyubskii





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